Symposium on

ADVANCES IN ELECTRON METALLOGRAPHY AND ELECTRON PROBE MICROANALYSIS

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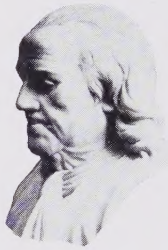

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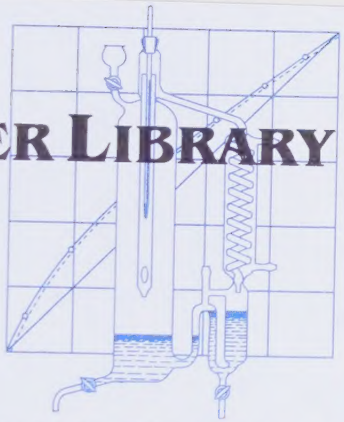
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SYMPOSIUM ON ADVANCES IN ELECTRON METALLOGRAPHY AND ELECTRON PROBE MICROANALYSIS

Sponsored by

SUBCOMMITTEE XI ON ELECTRON MICROSTRUCTURE OF

ASTM COMMITTEE E-4 ON ELECTRON METALLOGRAPHY

Held at

Atlantic City, N. J., June 28, 1960, and June 26, 1961

Reg. U. S. Pat. Off.

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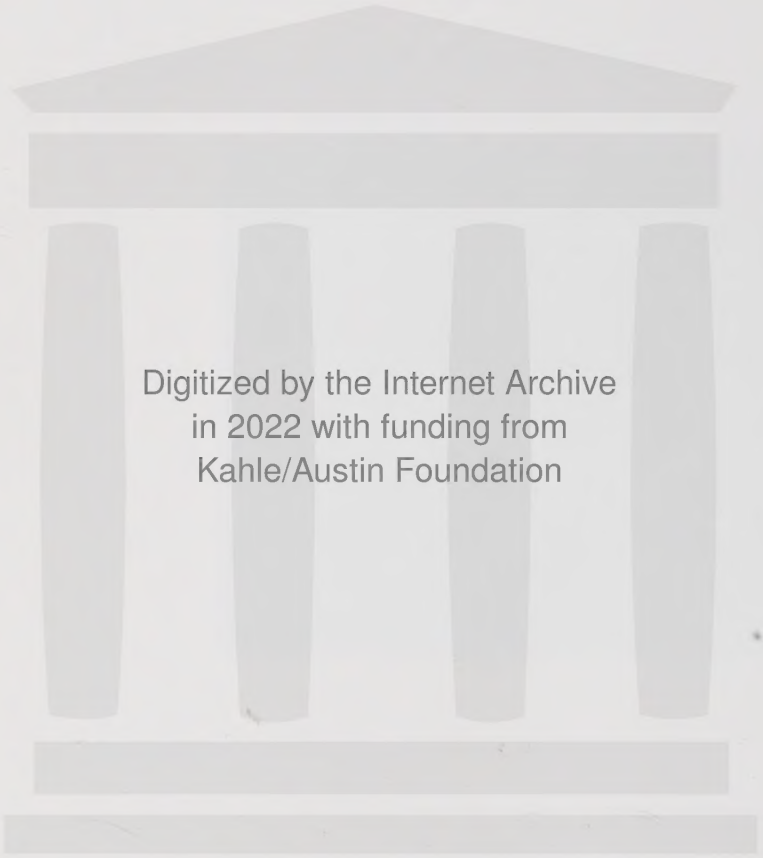
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Library of Congress Catalog Card Number: 62-18223

Printed in Baltimore, Md.
September, 1962

FOREWORD

This Special Technical Publication presents reports on new techniques and researches in the field of electron metallography and electron probe microanalysis. Included are papers presented in two technical sessions of ASTM under the sponsorship of Subcommittee XI on Electron Microstructure of Metals of ASTM Committee E-4 on Metallography. The first session was held in Atlantic City, N. J., Tuesday, June 28, 1960, during the Sixty-third Annual Meeting of the Society. The second session took place Monday, June 26, 1961, in Atlantic City, N. J., at the Sixty-fourth Annual Meeting of the Society.

In addition to the papers presented at these sessions, the First Progress Report of the Electron Transmission Microscopy Task Group of Subcommittee XI, entitled "Electron Transmission Microscopy of Metals" is presented in this volume. A survey paper, "Recent Advances in the Application of Electron Microscopy to the Study of Metals," by W. C. Bigelow, has been included because of the practical value of an extensive and timely review of this type to workers in the field. A "Classified Bibliography on Electron Probe X-ray Microanalysis," prepared by B. R. Banerjee (chairman), K. F. J. Heinrich, and F. B. Riggs of the Task Group on Electron Probe Microanalysis of Subcommittee XI is also included, again because of its timeliness in relation to an expanding interest in this field. Also included is "Effect of Surface Finishing on Development of θ' Phase in an Aluminum - 4 per cent Copper Alloy" by N. Takahashi and H. Kosuge.

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NOTE.—The Society is not responsible, as a body, for the statements and opinions advanced in this publication.

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SYMPOSIUM ON ADVANCES IN ELECTRON METALLOGRAPHY AND ELECTRON PROBE MICROANALYSIS

INTRODUCTION

By C. M. Schwartz[1]

This is the third ASTM Special Technical Publication presenting techniques developed for electron metallography. The present volume displays a continuation of the trend established in the previous volume, namely, the inclusion of a number of papers involving techniques other than conventional electron metallography. This increased coverage is a reflection of the broadened scope of activities of Subcommittee XI.

The techniques described in the first publications[2, 3] of this series were concerned mainly with surface replication for the study of metallurgical structure. The second publication[3] already demonstrated a diversification of workers' interests into the fields of transmission electron microscopy, electron diffraction, and electron probe microanalysis. This influence has been shown in the activities of Subcommittee XI, which has initiated task groups for cooperative study of techniques in each of these areas. The present volume includes the First Progress Report of the Task Group on Electron Transmission Microscopy of Subcommittee XI which provides information on thin film techniques for iron, stainless steel, and aluminum, and demonstrates the application of this method to the study of certain microstructural features, namely, lattice defects, subgrain boundaries, orientation, and structure. A bibliography of papers in the field of transmission electron microscopy is appended to the Progress Report.

Other contributions to the study of thin film electron metallography include papers by Banerjee, Capenos, and Hauser on techniques and observations on commercial 410 stainless steel; by Phillips demonstrating the direct observation of microstructure in metals sectioned by ultramicrotomy; and by Young, Melton, and Schwartz on zirconium and Zircaloy-2.

Interest in the application of electron probe microanalysis is evident in the paper by Ohh and Carroll, dealing with diffusion in the system iron-nickel, and that by Birks, describing a procedure for calculating element concentrations from the measured X-ray intensities. (This paper has been published elsewhere.[4]) The activities of the Task Group on Electron Probe Microanalysis of Subcommittee XI were presented at the Sixty-fourth Annual Meeting in a Progress Report on "Round-Robin Testing of a Niobium-Iron Diffusion Couple by

[1] Battelle Memorial Inst., Columbus, Ohio.

[2] Symposium on Techniques for Electron Metallography, *ASTM STP No. 155*, Am. Soc. Testing Mats. (1953).

[3] Symposium on Advances in Electron Metallography, *ASTM STP No. 245*, Am. Soc. Testing Mats. (1958).

[4] L. S. Birks, "Techniques for Calculating X-ray Intensities in the Electron-Probe Microanalyzer," *Journal of Applied Physics*, Vol. 31, p. 1297 (1960).

Electron Probe Analysis Methods." This effort is incomplete, however, and it is expected that the completed results will be reported in the future. A classified bibliography of electron probe microanalysis, prepared by members of this task group, however has been included in this volume.

To assist newcomers in the field and to provide an excellent source of information on the many facets of electron metallography, a review paper by Bigelow provides timely data on such subjects as instruments, techniques, and applications, together with an extensive list of references. Wilkins and Pence report on the structure of precipitation hardening stainless steels as observed by replica techniques. These particular alloys are now being examined by Subcommittee XI using transmission electron microscopy, and it is hoped that a report of this investigation will be published eventually. Microstructural evidence of tensile deformation of an age-hardened nickel-base alloy was observed by Madden, Bigelow, and Sponseller. A useful method for the removal of plastic backing films in certain techniques of replica preparation is described by Beals and Bigelow. The morphology of nitride precipitates in 12 per cent chromium stainless steels was investigated by Banerjee, Capenos, and Hauser, using extraction replica techniques.

Finally, two papers are presented, dealing with diffraction methods of structure analysis, which have in common the use of a focused electron beam available in these instruments. One is a paper by Beattie on electron diffraction intensities, which discusses the occurrence of "forbidden" reflections and its importance in interpretation of the data and in its utilization for structure analysis. Last but not least, the paper by Heise describes the very useful auxiliary application of the electron probe analyzer as a point source of strongly divergent characteristic X-rays to produce Kossel patterns. Applications to studies of crystal orientation and to determination of lattice constants are illustrated.

Subcommittee XI is currently engaged in transmission electron microscope studies of thinned precipitation hardening stainless and high-temperature alloy steels, in the development of techniques for electron probe microanalysis, and in the evaluation of techniques for electron diffraction. It is hoped that progress in these areas will be reported at future ASTM symposia.

ELECTRON TRANSMISSION MICROSCOPY OF METALS

First Progress Report of the Electron Transmission Microscopy Task Group of Subcommittee XI on Electron Microstructure of Metals, ASTM Committee E-4 on Metallography*

Subcommittee XI on Electron Microstructure of Metals of ASTM Committee E-4 on Metallography first became interested in direct transmission electron microscopy of metal foils in 1958, as a result of published reports of the successful transmission microscopy of aluminum and stainless steel. In these papers it was noted that dislocations and other lattice defects could be detected in the electron images. The subcommittee undertook to investigate the method in order to assess it in relation to established replica techniques. The results of this assessment are outlined in this report, the primary purpose of which is to provide a guide for metallographers as to the additional information that may be obtained by transmission microscopy. The difficulties and limitations of the method are also indicated, and some comments regarding the experimental techniques are included. It is not the purpose of this report to discuss in detail the interpretation of electron images of crystalline foils; this has been the subject of several recently published papers (see Bibliography, Appendix I[1]).

Standard specimens were prepared which have been examined by various subcommittee members. However, during the course of this work a large number of papers dealing with transmission electron microscopy of metal foils have been published. Thus the conclusions presented in this report are derived from published reports as well as from the results obtained by subcommittee members. It is emphasized that the technique discussed here is at present in a state of rapid development, and the purpose of presenting a report at this time is only to provide a tentative guide for metallographers who may be interested in using the transmission method.

In view of the fact that the literature dealing with this technique has accumulated rapidly during the past few years, it was felt that a bibliography would be useful at this time. This is included as Appendix I.[1]

Subcommittee XI Project and Results

The following samples, in the form of foil a few thousandths of an inch thick, were distributed to subcommittee members:

Stainless steel, type 316 cold rolled and recrystallized by heating at 1050 C for 30 min in vacuum, air cooled,

[1] See p. 19.

* Members and participants of this Task Group include: C. M. Schwartz (Chairman), Battelle Memorial Inst.; J. R. Mihalisin (Secretary), Research Laboratory, International Nickel Co.; F. W. Boswell (Report Editor), Department of Mines and Technical Surveys, now at The University of Waterloo, Waterloo, Ont.; V. A. Phillips, Research Laboratory, General Electric Co.; A. S. Turkalo, Research Laboratory, General Electric Co.; M. S. Hunter, Aluminum Research Laboratories, Aluminum Co. of America; and A. Szirmae, Fundamental Research Laboratory, U. S. Steel Corp.

Stainless steel—as above plus extended about 3 per cent

Iron (Ferrovac E, containing about 0.01 [illegible] per cent carbon)—cold rolled and recrystallized by heating at 650 C for 1 hr in vacuum,

Iron—as above plus cold rolled 4 per cent reduction in area,

Aluminum (99.99 per cent)—cold rolled, and

Aluminum (99.99 per cent)—recrystallized.

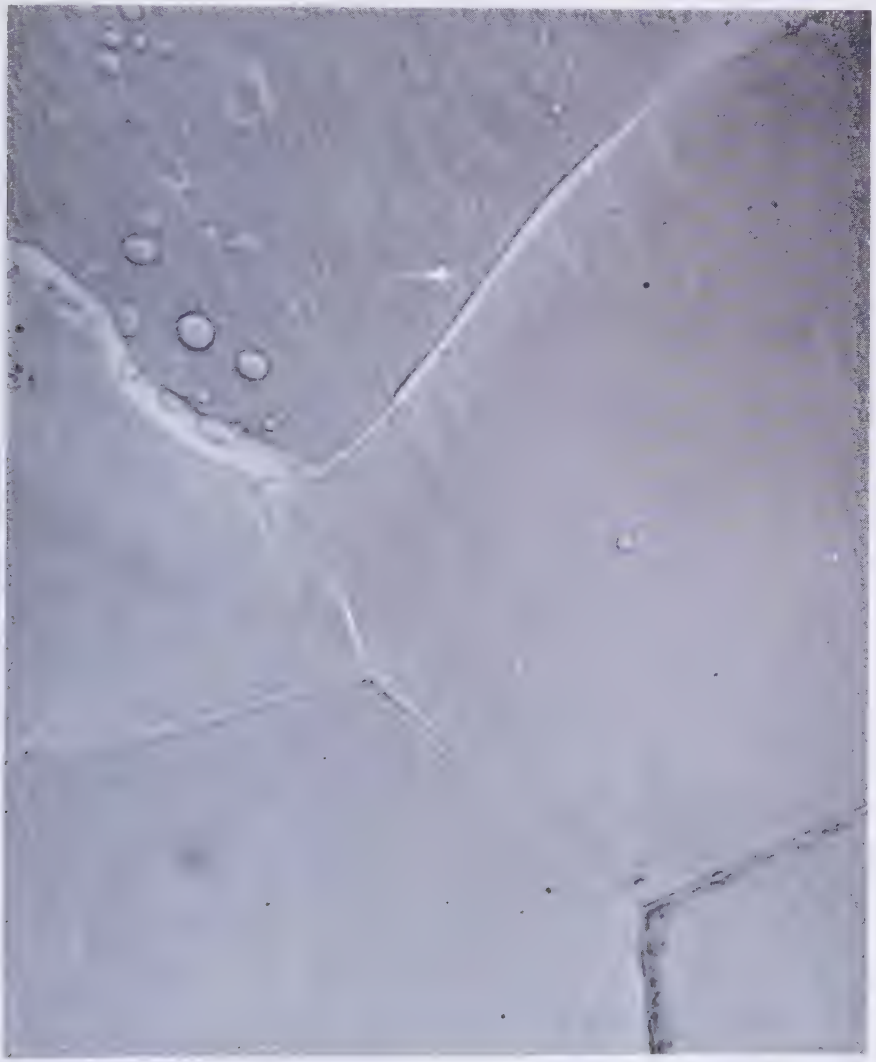
These specimens were examined in several different laboratories, using a variety of thinning techniques. The thinning procedures used are outlined in Appendix II.[2] Specimens should be rinsed immediately after polishing, given

Courtesy of Department of Mines and Technical Surveys, Ottawa.

FIG. 1.—Transmission Micrograph of Annealed Stainless Steel (×50,000).

[2] See p. 24.

a final rinse in methyl alcohol, and blotted dry on tissue. Suitable regions for electron microscopy can best be cut out by placing the specimen between two pieces of lens tissue and cutting with a razor blade. The specimen can then be gently pressed on an electroformed grid whose wires have previously been coated with a "tacky" cement or, alternatively, it can be placed between two grids of suitable mesh size. It is desirable that the specimen be in good thermal contact with the holder, to avoid the possibility of undue temperature rise.

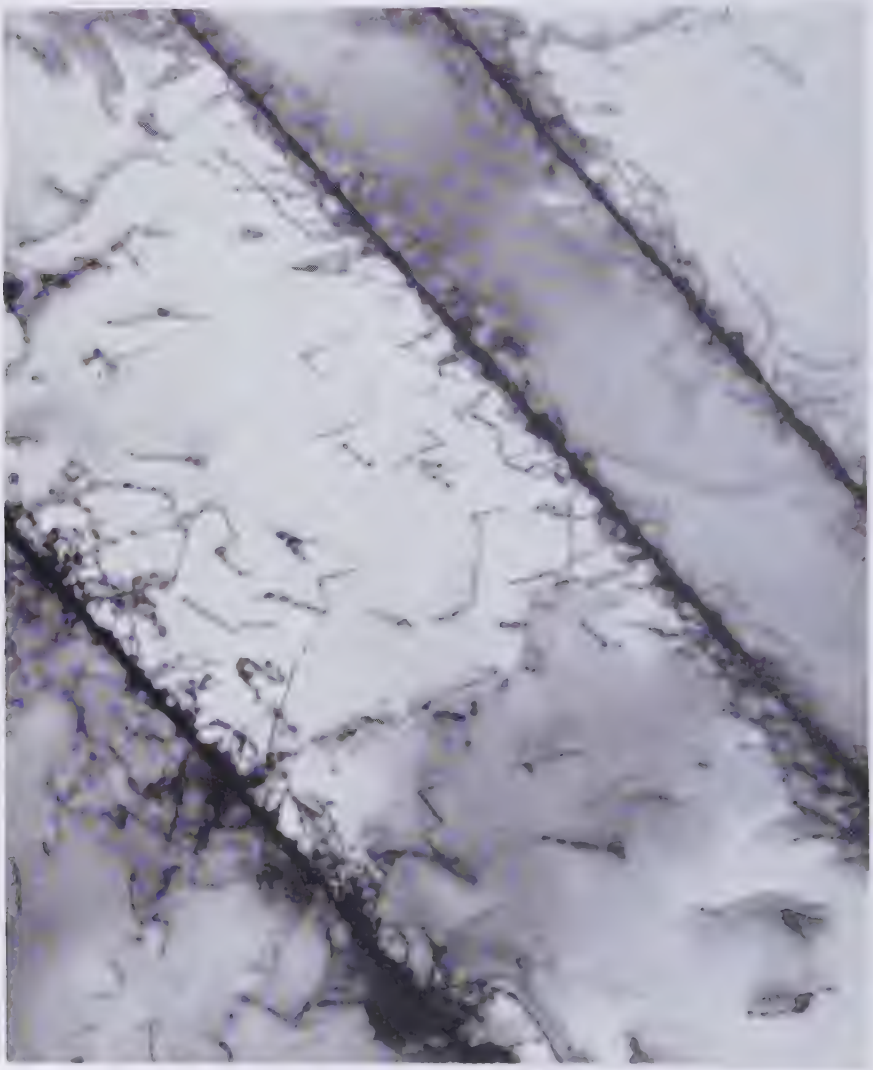


Courtesy of the International Nickel Co.

FIG. 2.—Replica of Annealed Stainless Steel.

Stainless Steel:

Typical results for stainless steel are shown in Figs. 1 to 4. Figure 1 is a transmission micrograph of annealed stainless steel foil. Very few dislocations can be detected, even when the foil is tilted. A few small dark spots can be detected which may be associated with dislocation loops or small particles of a secondary phase. Contrast across grains and twin boundaries is associated with the effect of orientation on the strengths of the diffracted beams. This contrast depends markedly on the orientation of



Courtesy of Department of Mines and Technical Surveys, Ottawa.

FIG. 3.—Transmission Electron Micrograph of Stainless Steel Extended 3 per cent (×50,000).

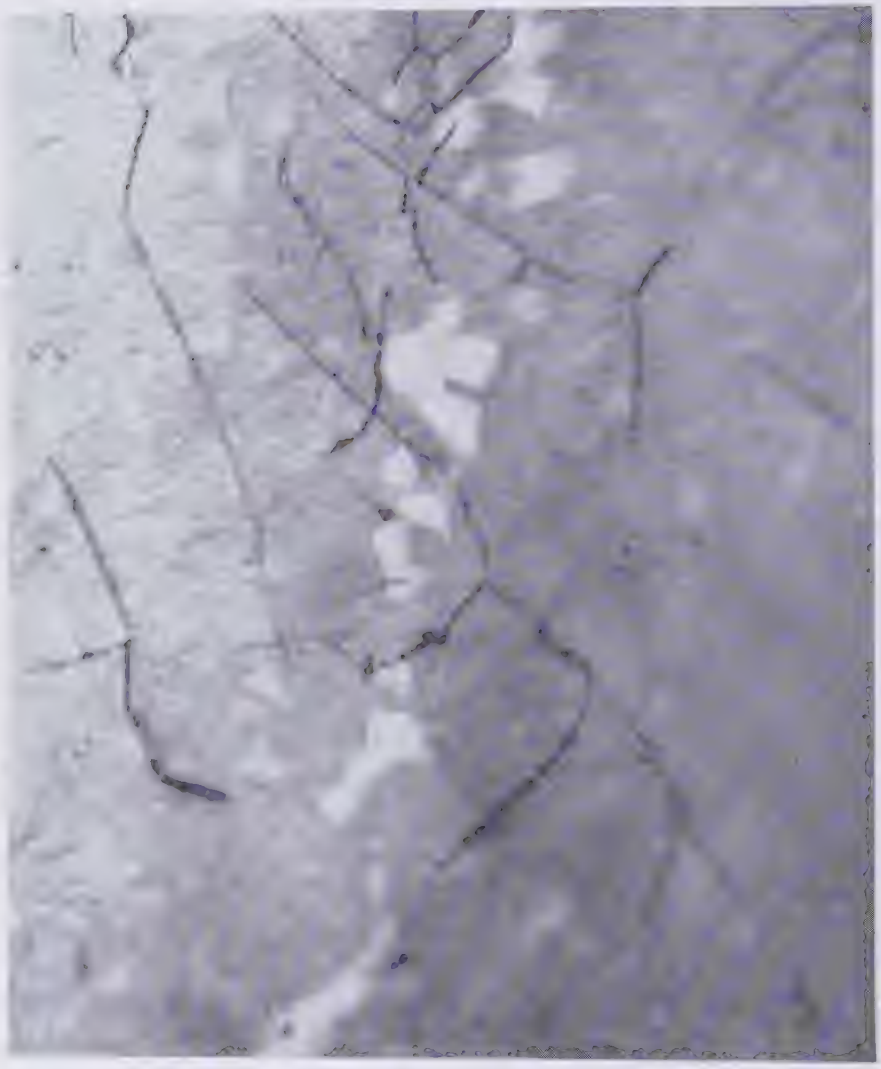
the specimen and can be altered by slight tilting. The fringes along the grain boundaries arise from interference effects

Courtesy of the International Nickel Co.

FIG. 4.—Replica of Stainless Steel Deformed 15 per cent (×25,000).

associated with the overlapping wedge-shaped crystals. A dry-stripped plastic surface replica from a polished and etched specimen of the foil is shown in Fig. 2. Here grain boundaries, twin boundaries, and inclusions can be recognized. Inclusions of the size shown in Fig. 2 are not likely to be detected by the transmission technique since holes would probably form at the inclusions during the thinning process.

A transmission micrograph of lightly deformed stainless steel is shown in Fig. 5. A large number of dislocations, some of them piled up at the long diagonal boundaries, may be observed. It is to be noted that some of the dislocations appear as smooth dark lines, while others appear as a jagged line or series of dots. These effects have been discussed in recent papers dealing with the theory of image contrast in electron micrographs of crystals. Figure 4 is a replica of stain-



Courtesy of the General Electric Co.

FIG. 5.—Transmission Micrograph Showing Dislocations in Recrystallized Iron Foil (× 40,000).

Note precipitation along some of the dislocations (see text for details).

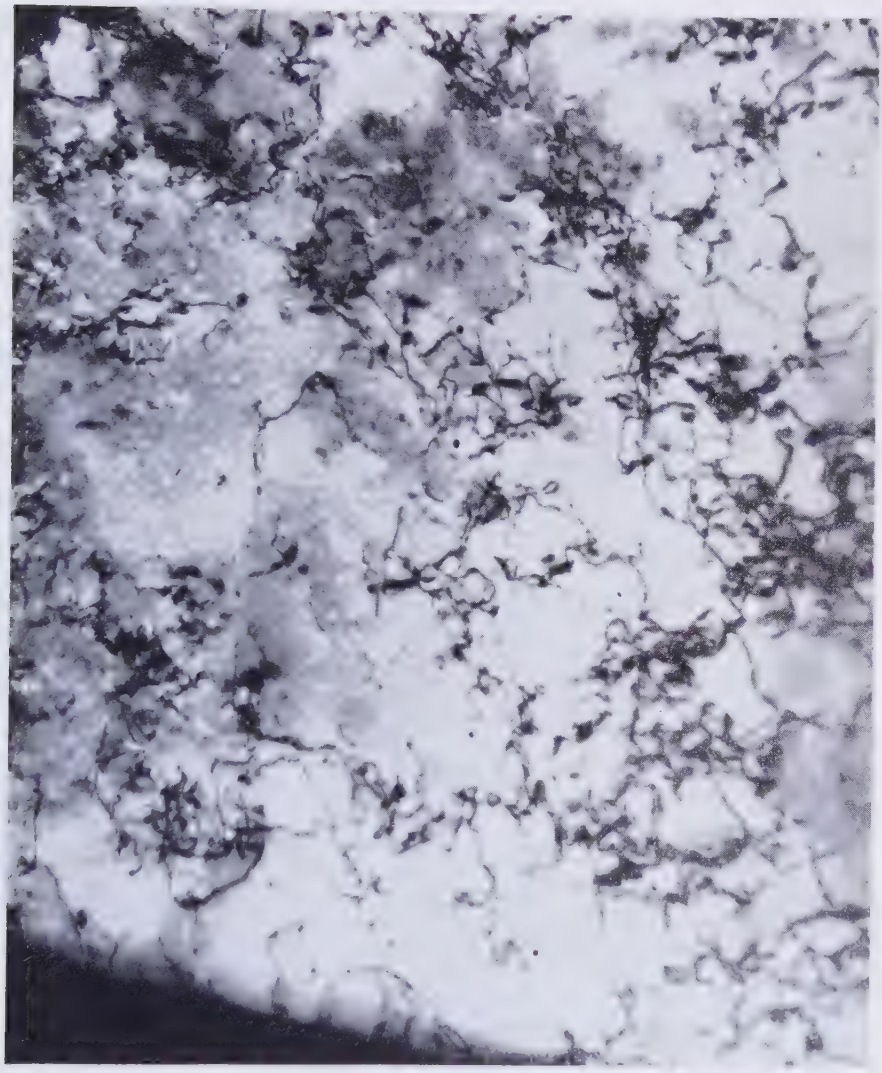
Courtesy of the Department of Mines and Technical Surveys, Ottawa.

FIG. 6. Transmission Micrograph of Recrystallized Iron Foil Aged at Room Temperature for 2 yr (see text) (×50,000).

less steel, deformed 15 per cent, and subsequently polished and etched. Deformation bands can be clearly seen in the replica. However it is clear from comparison with Fig. 3 (which has had only 3 per cent deformation) that the fine slip lines do not show in the replica. It is possible that the deformation lines in Fig. 4 are associated with the dark, straight, diagonal lines in Fig. 3. However, more detailed work would be required to establish the nature of the lines observed in Figs. 3 and 4. It may be noted that a first step in the analysis would require the determination of the orientation of the dark lines in Fig. 3.

Courtesy of the International Nickel Co.

FIG. 7.—Replica of Recrystallized Iron Foil (×5000).



Courtesy of Department of Mines and Technical Surveys, Ottawa.

FIG. 8.—Transmission Micrograph of Iron Foil Deformed 4 per cent by Rolling (×50,000)

This could be directly carried out by selected area electron diffraction.

Iron:

Results obtained on the iron foils are shown in Figs. 5 to 10. These results are somewhat complicated by the fact that the iron contained a small amount of carbon, with the result that iron carbide slowly grew in some of the foil over the two-year period of the subcommittee work. A transmission micrograph of recrystallized iron foil, taken a few months after the foil was recrystallized and air cooled, is shown in Fig. 5. The row of white patches appears to be a spurious effect associated with uneven surface attack during polishing or rinsing.

Several dislocations can be seen in this field and close inspection reveals a "sawtooth" effect along some of them. This

particles are now much more fully developed. It was established by selected-area electron diffraction that the plane

Courtesy of the International Nickel Co.

FIG. 9.—Replica of Iron Foil Deformed 4 per cent by Rolling (×5000).

effect is believed to have resulted from precipitation of iron carbide along the dislocations. A micrograph of a similar specimen taken after a period of two years is shown in Fig. 6. The iron carbide

of the foil was (100) in this case, and hence the iron carbide is in the form of disks lying in the three planes of this form. These particles are probably not cementite. A replica of the recrystallized

iron is shown in Fig. 7. The grains are clearly outlined and the etch attack depends on the grain orientation.

A transmission micrograph of iron deformed 4 per cent by rolling is shown in Fig. 8. Many dislocation loops resulting from dislocation glide may be seen. It should also be noted that no iron carbide particles can be detected even though the deformed foil had been stored at room temperature for about two years before thinning. It appears that the carbon must be distributed uniformly along the much greater length of dislocation line now present. Figure 9 shows a replica of the deformed iron. Little additional information is available as compared with Fig. 7, although the etch attack appears to be less uniform in Fig. 9, with more tendency to form shallow etch pits. Some of the pits appear to have a well-defined mark at their apex which indicates that they may be associated with a particle of some sort. Figures 10 (*a*) and (*b*) are transmission micrographs of the same field in a deformed iron foil. The specimen was tilted slightly between the two exposures and it is interesting to note the typically large effect of this tilting on the dislocation images. In Fig. 10(*a*) the dislocations in the lower grain are generally sharp while those in the upper grain are diffuse. In Fig. 10(*b*) the dislocations in the lower grain are faint and diffuse while those in the upper grain are sharp, although many consist of double lines. In addition, dislocations can be seen in the upper grain of Fig. 10(*b*) which are not present in Fig. 10(*a*).

Aluminum:

Figure 11 is a micrograph of recrystallized aluminum foil. A small group of dislocations can be seen in one of the grains, but the over-all dislocation density is not more than 10^7 per sq cm. The fact that all three grains transmitted about the same proportion of the incident electrons is a coincidence associated with the particular orientations involved—generally there is marked contrast between different grains. The double line along the grain boundary is an interference effect. Cold-rolled aluminum foil is shown in Fig. 12. Here many dislocations may be seen and there is a very marked tendency for these dislocations to be arranged in walls separating subgrains of the order of 1μ in size. The contrast at the boundaries is complex—in some cases individual dislocations appear to be resolved but in general it is difficult to be certain that individual dislocations rather than interference fringes are being observed. To elucidate the structure of a particular boundary, observations on the change of contrast on tilting, together with electron diffraction data from the area involved, are required.

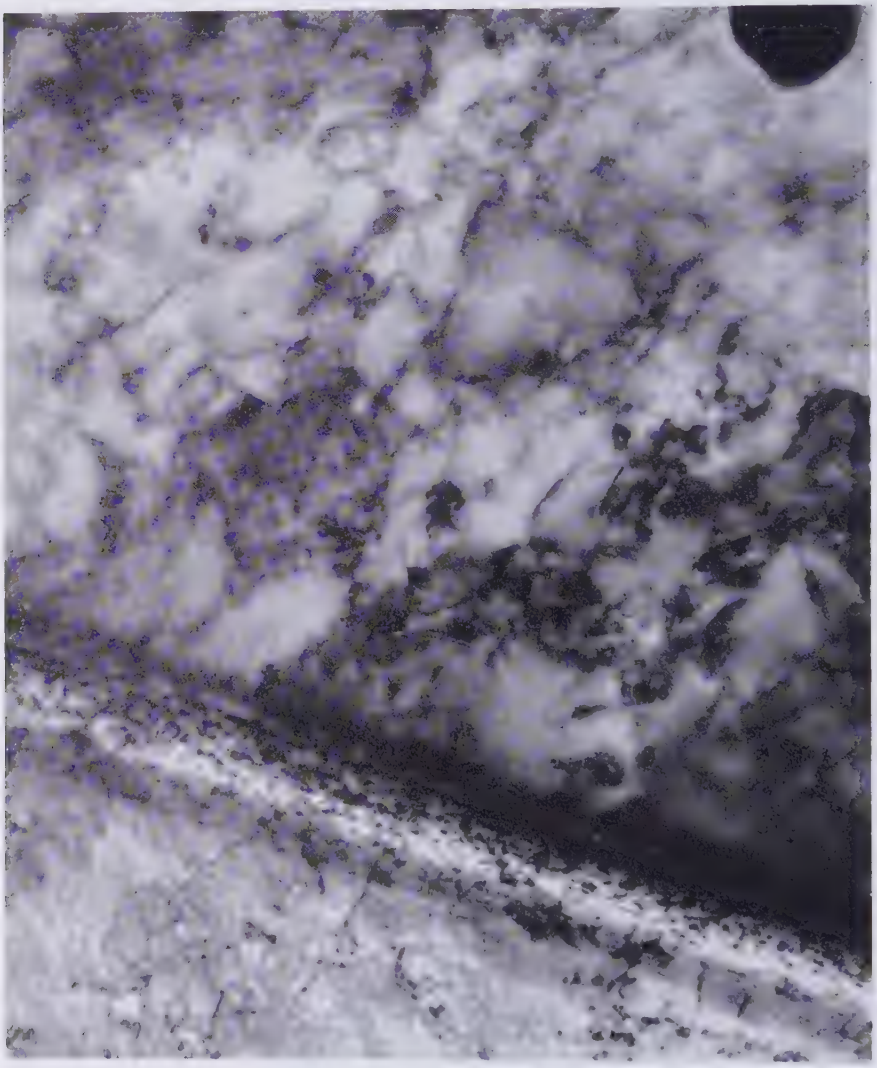
Discussion and Conclusions

In general, more time must be spent to prepare specimens for transmission microscopy than to prepare surface replicas. This is particularly so if the specimen is more than a few thousandths of an inch in thickness, as special thinning methods must be devised. On the other hand, when a program can be designed so that foil specimens less than 0.010 in. in thickness are available, then once a suitable electropolishing technique has been found it is possible to prepare transmission specimens in a few minutes.

At this stage of development of the technique the experience of the subcommittee indicates that there is no advantage in recommending specific thinning methods, other than to state that electrolytic methods appear to be the most generally satisfactory. The geometrical arrangement of the electropolishing setup and the particular elec-

trolyte used are of secondary importance, provided the electrolyte chosen is capable of giving a bright polish. Experience in establishing optimum polishing conditions and stopping the polishing at the appropriate time are important factors.

A comparison of the advantages and limitations of the transmission method compared to standard replica methods is given in Table I. If the investigation is concerned simply with a comparison of the distribution of phases in a series of

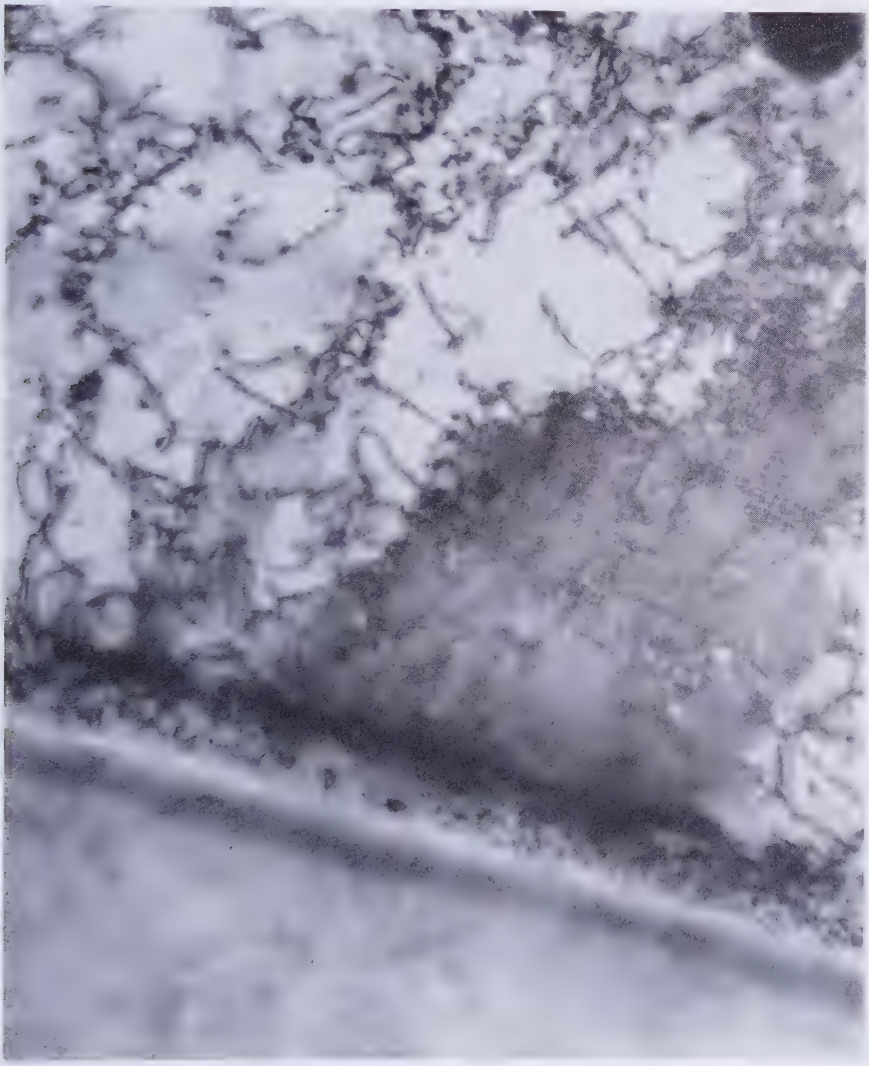


Courtesy of the Department of Mines, Ottawa.

(*a*) Dislocations in lower grain are sharp while those in upper grain are diffuse.

FIG. 10.—Transmission Micrographs of Iron
The specimen was tilted

specimens and provided the secondary phase can be delineated by etching and resolved in a replica, then a replica is required, an extraction replica is adequate provided an etchant can be found to dissolve the matrix preferentially. The



Courtesy of the Department of Mines, Ottawa

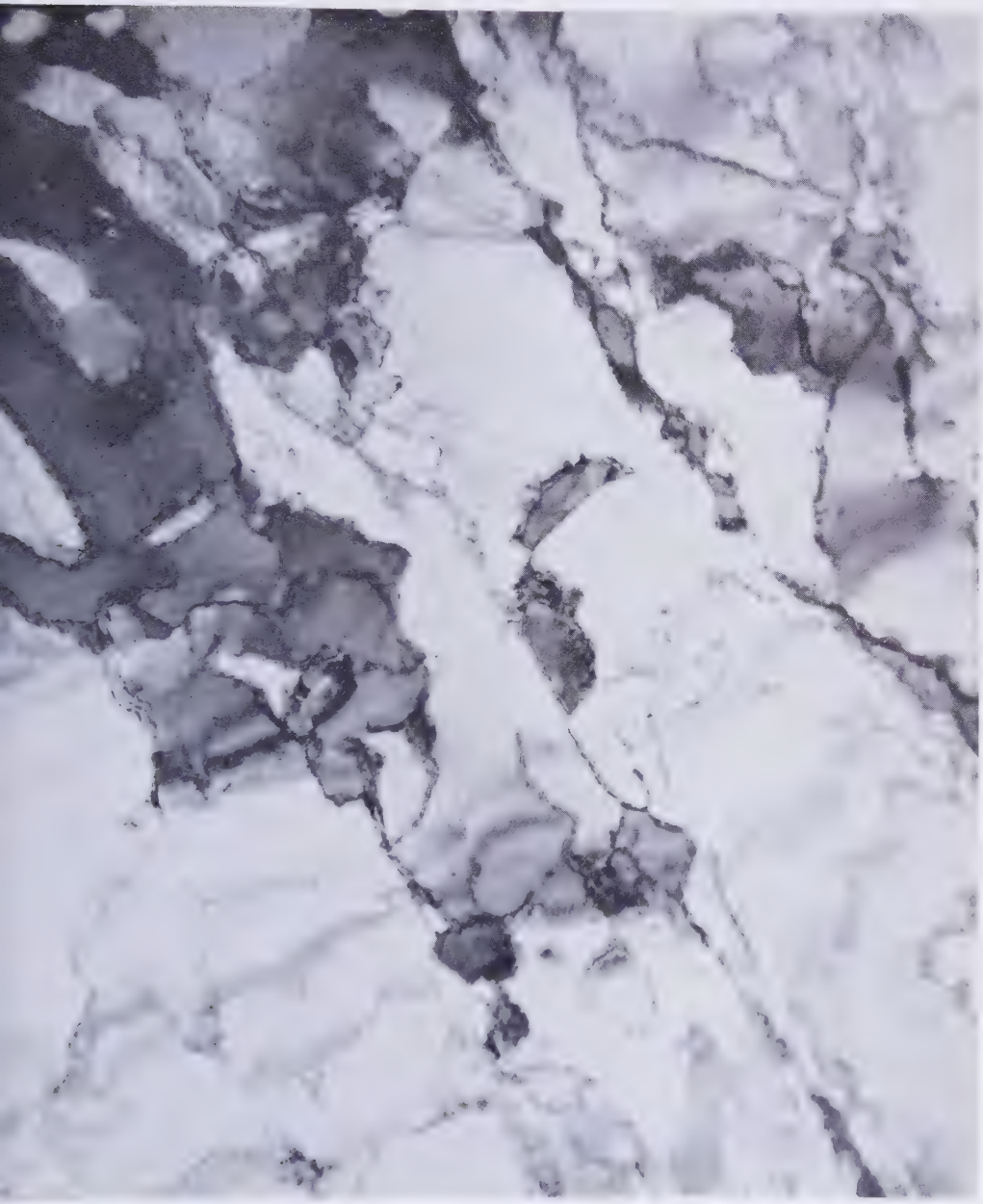
(*b*) Dislocations in lower grain are diffuse while those in upper grain are sharp.

Foil Deformed 4 per cent by Rolling (×50,000).
between the two exposures.

method is probably the quickest and simplest approach. If identification of secondary phases by electron diffraction major advantage of the transmission technique is that additional information relating to lattice defects, subgrain struc

Courtesy of the Aluminum Co. of Ame

FIG. 11.—Transmission Micrograph of Recrystallized Aluminum Foil (×20,000).



Courtesy of the Aluminum Co. of America

FIG. 12.- Transmission Micrograph of Cold-Rolled Aluminum Foil (×10,000)

TABLE I.—COMPARISON OF TECHNIQUES IN ELECTRON METALLOGRAPHY.

	Plastic and Carbon Replicas	Carbon Extraction Replicas	Direct Transmission Microscopy
Time	Minimum in general	Somewhat greater than for ordinary replica	Depends on the electropolishing characteristics and form of specimen
Range of applicability	Wide	Depends on relative etching of different phases	Any specimen that can be electrolytically polished without severe pitting
Information obtainable	1. Size, shape, and distribution of secondary phases over 100 Å in size 2. Size and shape of grains 3. (Subgrain structure where this can be developed by etching)	1. Size, shape, and distribution of secondary phases with better resolution than for ordinary replicas 2. Size and shape of grains 3. Identification of extracted phases by electron diffraction	1. Nature and density of lattice defects 2. Size and shape of grains 3. Orientation of grains by electron diffraction 4. Size, shape, and distribution of secondary phases 5. Identification of secondary phases by electron diffraction 6. Orientation of secondary phases by electron diffraction 7. Subgrain shapes and sizes 8. Average misorientation of subgrains by electron diffraction

ture, crystal structure, and orientations can be obtained. In particular, the growth mechanism of the particles and the relation of particle growth to lattice defects can be determined. Thus transmission microscopy is a new technique which substantially increases the scope and potentiality of electron metallography. The choice of technique in a specific case depends primarily on the information desired concerning the specimen.

APPENDIX I

BIBLIOGRAPHY OF PAPERS RELATING TO TRANSMISSION ELECTRON MICROSCOPY OF THIN CRYSTALLINE SPECIMENS UP TO JUNE, 1960

General Articles:

R. Castaing and Paul Laborie, "Direct Examination of Metals by Transmission in the Electron Microscope," *Comptes rendus*, No. 21, p. 1330, Nov. 23, 1953.

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APPENDIX II

THINNING TECHNIQUES USED BY SUBCOMMITTEE XI MEMBERS

General Electric Research Laboratory (V. A. Phillips):

A modified Disa Electropol Type 53A was used to polish a region of about 1 cm in diameter. After the specimen was brightly polished on one side and reduced to about one half of its original thickness it was turned over and polishing continued until holes appeared. For pure iron and stainless steel the electrolyte was as follows:

78 ml perchloric acid; 602, specific gravity 1.54,
120 ml distilled water,
700 ml ethanol, and
100 ml butylcellosolve.

NOTE.—The perchloric acid should be added to the previously prepared mixture of the other ingredients immediately before use.

General Electric Research Laboratory (A. S. Turkalo), United States Steel Corp. Fundamental Research Laboratory (A. Szirmae), and the International Nickel Co., Research Laboratory (J. R. Mihalisin):

Iron specimens were thinned essentially by the Bollmann technique using the following electrolyte:

133 ml glacial acetic acid,
25 g CrO_3, and
7 ml H_2O.

Specimens were rinsed in distilled water to which a few drops of ammonium hydroxide were added. They were then rinsed in ethyl alcohol. While in the alcohol, pieces suitable for electron microscopy were cut out. These were placed in a 5 per cent solution of hydrochloric acid in ethyl alcohol for 20 sec to remove any surface film. They were then rinsed again in alcohol and blotted dry on bibulous paper.

Department of Mines and Technical Surveys, Ottawa (F. W. Boswell):

A modified Bollmann technique was used. The details have been published by Boswell and Smith.[3]

International Nickel Co., Research Laboratory (J. R. Mihalisin):

The stainless steel foil was polished in an electrolyte of the following composition:

Concentrated H_2SO_4 ..... 720 ml,
H_2O ..... 70 ml, and
Glycerin ..... 200 ml.
Room temperature, 6 to 10 v.

Aluminum Company of American Research Laboratories (M. S. Hunter):

The technique used to thin pure aluminum is described in detail by Robinson.[4]

[3] F. W. C. Boswell and E. Smith, "Examination of Metals by Transmission Electron Microscopy," Symposium on Advances in Electron Metallography, *ASTM STP No. 245*, Am. Soc. Testing Mats., p. 31 (1958).

[4] D. L. Robinson, *Journal of Applied Physics*, Vol. 29, p. 1635 (1958).

APPENDIX III

METALS AND ALLOYS THINNED BY ELECTROLYTIC OR CHEMICAL TECHNIQUES FOR ELECTRON MICROSCOPY—ACCORDING TO PUBLISHED DATA TO JUNE 1960

Metal	References
Aluminum	**1, 4, 8, 10, 11, 12, 17, 18**
Aluminum-copper	**10, 12, 16**
Aluminum-magnesium	**12, 16**
Aluminum-manganese	**12**
Aluminum-silver	**4, 16**
Aluminum-zinc	**16**
Aluminum-Mg_2Si	**13**
Beryllium	**1**
Beryllium	**14**
Cobalt	**17**
Copper	**15, 17**
Copper-beryllium	**12**
Copper-beryllium-nickel	**12**
Alpha brass	**4, 17**
Bronze	**1**
Germanium	**7**
Gold	**15**
Iron	**4, 5, 17**
Steel	**1, 9**
Silicon steel	**17**
Stainless steel	**1, 2, 4, 17**
Magnesium	**18**
Nickel	**3, 17**
Nickel-chromium-cobalt	**1**
Silicon	**7**
Tin	**6**
Titanium-copper	**12**
Titanium-aluminum	**12**
Uranium	**12**

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TRANSMISSION ELECTRON MICROSCOPY OF TYPE 410 STAINLESS STEELS*

By J. M. Capenos,[1] J. J. Hauser,[1] and B. R. Banerjee[1]

A thin metal film for direct-transmission electron microscopy was first prepared by Heidenreich (1),[2] using an electrolytic thinning technique based on the principles of electropolishing. Since that time, various modifications of the electrolytic thinning technique as well as other methods have been developed which involve chemical dissolution (2), mechanical deformation (2), ion bombardment (3), vacuum deposition (4), or chemical etching (5). Of all these methods, electrolytic thinning has been the most successful approach and is also the most widely applicable technique because it introduces least deviation in structure from the bulk material. Although the precise mechanism of electrolytic thinning has not been clearly established, many improvements in technique have been empirically devised. For example, preferential thinning at the specimen edges has been reduced by coating the edge with nonconductive lacquers, and by using point-cathode geometry (6). These developments were recently reviewed in detail (7).

A two-step electrolytic process using a perchloric-acetic acid electrolyte was the most satisfactory for rapidly and reproducibly thinning type 410 stainless steels. This technique—involving two separate cells having different electrolyte concentrations, electrode geometry, and cell potentials—produced much better results than modifications of electrode spacing, electrode geometry, or voltage adjustments made within a single cell. This technique permitted transmission electron microscopy of all structural details in quenched martensitic steels and also of minute structural details such as dislocations and subgrain boundaries in steels annealed at subcritical temperatures.

Although dislocations have been observed by transmission electron microscopy in several face-centered cubic metal systems, pure iron is the only body-centered cubic metal in which dislocations have been observed by this technique; however, results of this latter work are yet unpublished except for a brief reference to them (8).

Test Procedure

Sheets of commercial type 410 stainless steel 0.034 in. thick were cold rolled to 0.003 in. thickness. One-inch square specimens were cut from these rolled-thin sheets, which were then heat-treated in a tube furnace with a flowing argon atmosphere; the atmosphere should be pure enough to prevent observable surface reactions.

The heat-treatment consisted of austenitizing at 1800 F for 1 hr and oil

* Presented at a Technical Session during the Sixty-third Annual Meeting of the Society, June, 1960.

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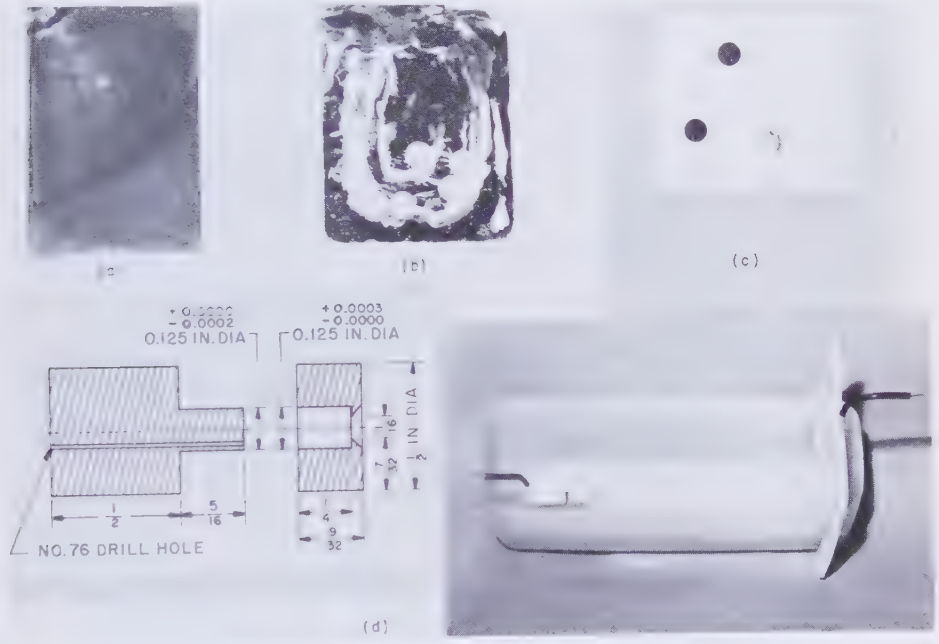
[2] The boldface numbers in parentheses refer to the list of references appended to this paper.

quenching to produce the martensitic structures. The austenitizing treatment was followed by a 2-hr subcritical anneal at 1300 and 1450 F to prepare the specimen so that dislocations and substructures in the ferrite could be observed.

The steel examined had the following composition: chromium, 11.94 per cent; carbon, 0.11 per cent; manganese, 0.41 per cent; phosphorus, 0.010 per cent; sulfur, 0.015 per cent; silicon, 0.25 per cent; nickel, 0.09 per cent; copper, 0.09 per cent; molybdenum, 0.05 per cent; tin, 0.01 per cent; aluminum, 0.01 per cent; lead, 0.002 per cent; and nitrogen, 0.036 per cent.

Preliminary Electrothinning:

The first step in electrolytic thinning included use of 10 per cent perchloric acid (60 per cent concentration) in acetic acid electrolyte. The specimen (Fig. 1(*a*)) was vertically suspended, by a 0.02-in. platinum wire, midway between two flat stainless steel cathodes, with 1-in. spacing between the specimen and each cathode. Preliminary thinning was done in this cell, using a cell potential of 30 to 35 v and an anode-current density of 1 to 1.5 amp per sq in.; under these conditions, rapid surface attack was obtained. Because of the cell geometry, polishing action was most vigorous at the specimen edges. As soon as excessive thinning was observed around the periphery, a commercial insulating lacquer—Polystyrene-Q dope[3]—was applied around the specimen edges in the



(*a*) Specimen before electrothinning.
(*b*) Specimen after preliminary thinning.
(*c*) Punched out disks.
(*d*) Modified Heidenreich holder for final electrothinning.

FIG. 1. Typical Specimens and Electrothinning Apparatus.

[3] General Cement Manufacturing Co., Rockford, Ill.

form of a picture frame. The painted specimen was inserted into the electrolyte by inverting it, end for end, so that the portion of the specimen which was formerly at the top was now at the bottom of the cell; this was done to compensate for enhanced attack at the top of the specimen caused by downward gravity flow of the viscous layer. Picture-frame coating, inverting of specimen, and polishing were repeated three to five times until the specimen center was considerably less than 0.001 in. thick; the entire preliminary thinning took about 2 to 3 min. At this point, perforations appeared at various points on the surface, particularly near the edges (Fig. 1(*b*)).

Final Electrothinning:

The second step in electrolytic thinning was begun by punching out from the thinnest areas of the prethinned specimen (Fig. 1(*b*)) $\frac{1}{8}$-in. diameter disks (Fig. 1(*c*)) suitable for direct insertion into the electron microscope specimen holder. These disks were placed in a Heidenreich-type (1) Teflon specimen holder (Fig. 1(*d*)).

The sketch in Fig. 1(*d*) shows pertinent dimensions of this holder. The holder consists of two parts: a cylinder provided with a reduced segment having a $\frac{1}{8}$-in. diameter and a friction-fitted cap. A small cylindrical hole drilled through the cylinder permits insertion of a 0.02-in. diameter platinum wire for making electrical contact with the specimen. The specimen is placed in the well, provided in the cap, and a 20 mil thick platinum backing disk of $\frac{1}{8}$-in. diameter is placed over the specimen. The cap, containing both specimen and backing disk, is then pushed over the reduced segment of the cylinder, and the combination is firmly pressed together to make good electrical contact with the slightly protruding platinum wire. The presence of the backing disk helps substantially to reduce rounding of the edges of perforations; a similar effect has been previously reported (9).

The anode cylinder is placed horizontally in the electrolytic cell so that the specimen surface is vertical. The cathode consists of a 0.02-in. diameter platinum wire that protrudes from a Teflon sheet (Fig. 1(*d*)); the anode-cathode spacing is about 3 to 4 in. The electrolyte is 4 per cent perchloric acid in acetic acid, contained in a rectangular cell; cell potential of 80 v and anode-current density of about 30 amp per sq in. were optimum. Specimens were thinned, in this second step, until 25 to 50 per cent of the exposed area had holed through, leaving extensive thin regions which were satisfactory for transmission microscopy.

Initial thickness of the disk seemed to be the most important factor determining the extent of satisfactory thin areas obtainable in the second step. If the initial thickness of the disk exceeded 0.001 in., satisfactory thin areas were seldom obtainable because holes appeared preferentially around the periphery, and the central portion of the specimen fell out of the holder before it was adequately thinned. If the disks were considerably less than 0.001 in. thick, there was no particular preferred region of attack in the second step; this was probably because of the uneven thickness of the prethinned disk, inherited from the first step. In the second step, thinning only one side of the specimen through the use of a backing plate, which also equalizes surface-current distribution after the specimen was perforated, was better than thinning from both sides, regardless of cathode geometry.

A Phillips EM100B instrument was used for all of the electron microscopy.

TEST RESULTS

The fine structural details of a type 410 stainless steel, in both quenched martensitic and subcritical annealed specimens, were examined by transmission electron microscopy, using this specimen preparation technique.

Martensitic Specimens:

During electropolishing, foils with quenched martensitic structures in-

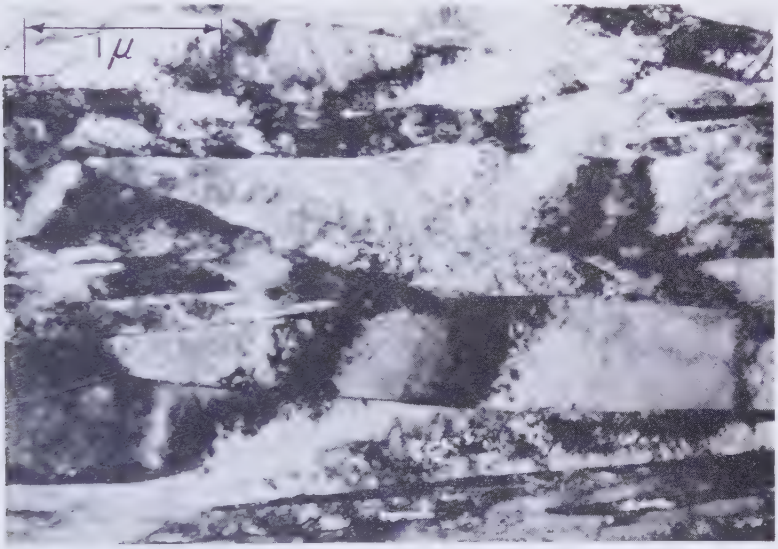


FIG. 2. -Specimen (Oil Quenched from 1800 F) Showing Martensite Plates. Broad interference fringes are seen within martensite lath.

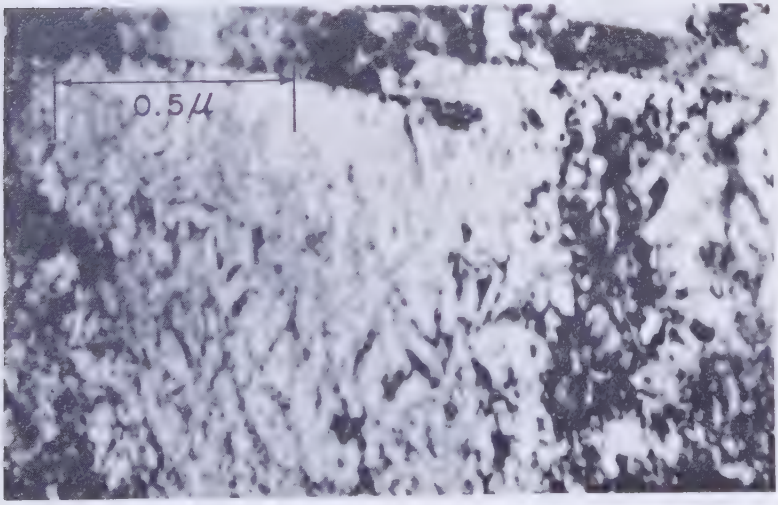
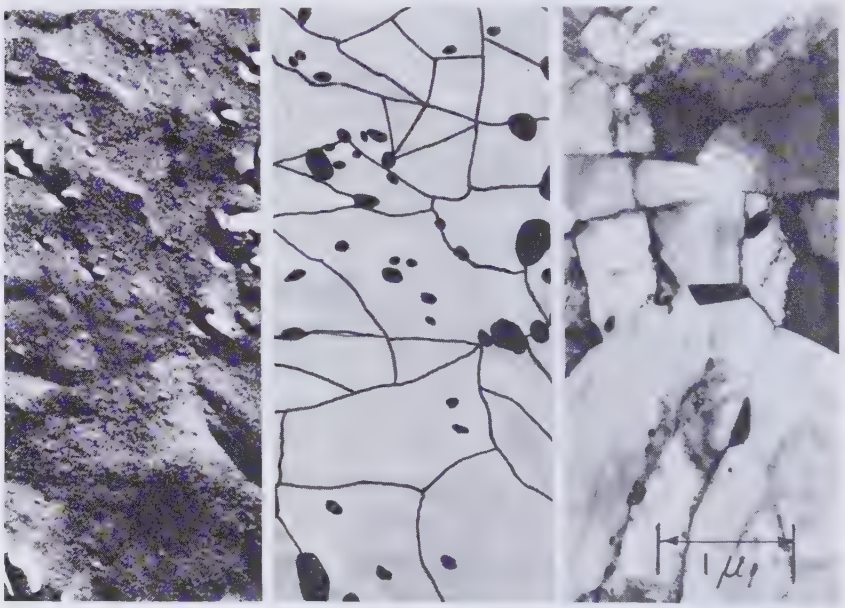


FIG. 3.—Specimen (Oil Quenched from 1800 F) Showing Irregular Dislocation Networks in Martensite.

variably thinned in an uneven manner. Figure 2 shows some of the typical interference fringes caused by this uneven thinning; a pair of broad vertical fringes is seen in the martensite lath at the center of the micrograph.

The uneven thinning within a single martensite lath may be caused either by the interstitial elements segregating on a submicroscopic scale or by a heterogeneous strain distribution. The microsegregation of interstitial elements may be caused by the freezing of atomic clusters formed during the austenitizing treatment; however this explanation is unlikely because the uneven thinning behavior persists upon tempering the quenched specimens to temperatures where microsegregation of interstitial elements would be rapidly eliminated by diffusion. The heterogeneous strain theory is favored because the austenite-to-martensite shear transformation, which retains the identity of close-packed rows of atoms, must involve a nonhomogeneous shear to account for the experimentally observed crystallographic relationships. This shear could introduce heterogeneous strains, which in turn could cause the observed uneven thinning of the quenched martensite specimens.



Shadowed replica. Tracing superposed. Thin section.

FIG. 4.—Subgrain Structure in Replica and Transmission Specimens (Quenched and Subcritical Annealed at 1300 F for 2 hr).

Irregular dislocation networks (Fig. 3) are the first observations of such networks in freshly quenched martensite; they are probably related to the same nonhomogeneous shear. The restraint imposed by the austenite surrounding a region transforming to martensite would introduce additional nonhomogeneous strain components, which—though small in thin specimens—may not be negligible in bulk specimens.

In some small regions parallel stria-

tions, spaced about 200 Å apart, were also observed (Fig. 2). The striations may be related to partial dislocations formed during the martensitic transformation; similar striae parallel to (112) planes were recently reported in iron-nickel alloys (10) and in thin foils of evaporated iron-carbon alloys (11).

Subcritical Annealed Specimens:

When the quenched specimens are subcritical annealed at high enough temperatures to complete the precipitation and agglomeration of carbides, the ferrite lattice fragments into substructures. These substructures are bounded by low-angle dislocation boundaries which can be clearly revealed by transmission electron microscopy. Although evidence of such substructures has been previously obtained by shadow-replica techniques, the substructures were mostly unrecognized and sometimes erroneously attributed to replica artifacts. Figure 4 shows, on the left, a uranium-shadowed replica in which the tilting of subgrains was revealed by maximizing photographic contrast. However, the transmission micrograph of a similarly heat-treated specimen, on the right of Fig. 4, clearly and unequivocally shows the subgrains of 0.4 μ average size. Tracing the boundary outlines of the replica micrograph, as shown in the central photograph with tracing superimposed, easily establishes the identity of structural observations by the two techniques.

Figure 5 shows a tilt boundary with the dislocations, in the boundary, perpendicular to the foil thickness; the boundary dislocations have an average spacing of 280 Å. Buckling of the foil has produced a visual image of a cusp at the center of the tilt boundary; the slight angular tilt shows the dislocations, in the form of short parallel lines with spacing similar to the dots in the boundary region below the cusp. Buckling of the foil in the region of the cusp is also shown by pronounced interference fringes, which are seen across the center of the boundary when the specimen is slightly tilted in the microscope.

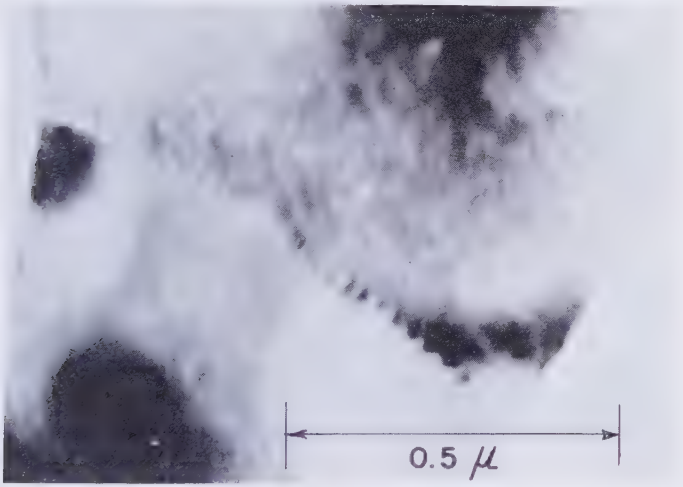


FIG. 5. Specimen (Quenched and Subcritical Annealed at 1450 F for 2 hr) Showing Tilt Boundary with Dislocations Perpendicular to Foil Thickness.

Figure 6 shows a tilt boundary with the dislocations inclined to the foil surface, a portion of a twist boundary, and several individual dislocations. Individual dislocations within the matrix, as well as dislocations ending in the subboundary are seen. This figure also shows some coarse-carbide precipitates in the field of view.

A systematic study of tempering reactions and dislocation interactions is currently in progress using the technique established.

Although dislocations have been observed by transmission electron microscopy in several face-centered cubic metal systems, this study of dislocations in type 410 stainless steel represents the first such published effort with a commercial body-centered cubic steel structure.

Irregular-dislocation networks have been observed, for the first time, in a freshly quenched martensitic structure.

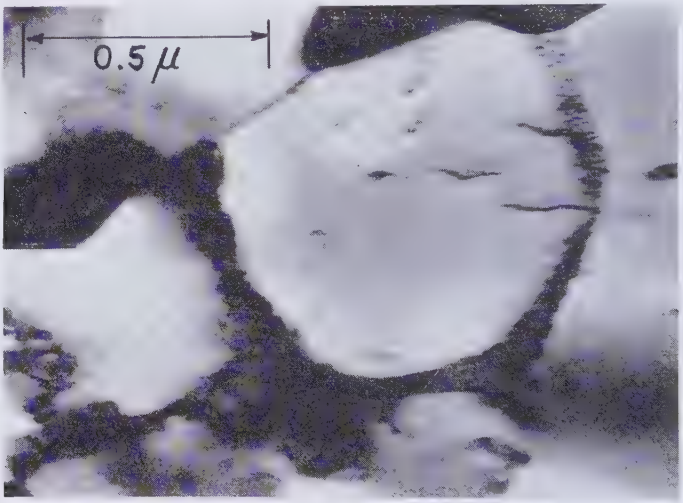


FIG. 6. Specimen (Quenched and Subcritical Annealed at 1300 F for 2 hr) Showing a Tilt Boundary with Dislocations Inclined to Foil Surface, a Portion of a Twist Boundary, and Several Individual Dislocations.

SUMMARY

A two-step electrolytic process, using a perchloric-acetic acid electrolyte, was developed for satisfactorily thinning type 410 stainless steels to permit transmission electron microscopy.

Substructures of 0.4 μ average size, with low-angle dislocation boundaries, were observed after a subcritical anneal.

Acknowledgment:

The authors are happy to acknowledge the able assistance of F. S. Snyder both in technique development and in subsequent specimen preparation.

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DIRECT OBSERVATIONS ON STRUCTURE OF ULTRAMICROTOMED METALS AND ALLOYS*

By V. A. Phillips[1]

Synopsis

Slices 100 to 600 Å thick were cut in an ultramicrotome from a variety of nonferrous metals and alloys and examined in an electron microscope. Microtoming appears to introduce high densities of dislocations which anneal out rapidly in the case of low-melting-point materials. High densities of "fault bands" are observed in certain grains of copper and silver. Particles as small as 7 to 20 Å thick by 70 Å or more long may readily be detected, together with the coherency strains round them. Fine holes may also be examined.

For direct examination in an electron microscope, foils <2000 Å in thickness are required. Even at 100 kv it is desirable that the foils should be considerably thinner than 2000 Å since the image quality tends to deteriorate progressively with increase in thickness due to diffuse scattering of electrons. For many purposes an optimum thickness is from 300 to about 600 Å. The ultramicrotome offers a speedy and direct method of obtaining thin foils from bulk specimens of single- and multiphase materials. Although most workers have so far employed electropolishing techniques for this purpose (1),[2] multiphase alloys are inherently difficult to thin electrolytically and the method is more time-consuming. In addition it is difficult to obtain large areas of uniform thickness by electrolytic means for examination.

The object of the present work was to explore the possibilities of microtoming and in particular to see whether metallurgically significant structures of bulk materials could be revealed by this technique in conjunction with a high-resolution electron microscope. It was not clear from previous work how far the cutting operation would damage the material structures, and it was not known whether or not high dislocation densities would be produced by cutting.

Previous Work

Haanstra (2) developed an ultramicrotome on which he successfully cut pure aluminum using a diamond knife. Fernandez-Moran (3) also developed an ultramicrotome on which he was able to cut aluminum, germanium, and uranium using a diamond knife which he developed (4,5). Reimer (6,7) has cut aluminum, nickel, iron, copper, gold, silver, palladium, platinum, and the 2-phase aluminum alloys with 4 and 33 per cent copper. He claims also to have cut cobalt, cadmium, and zinc, although no micrographs were included in his report.

* Presented at a Technical Session during the Sixty-third Annual Meeting of the Society, June, 1960.

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[2] The boldface numbers in parentheses refer to the list of references appended to this paper.

EXPERIMENTAL TECHNIQUE

A Leitz ultramicrotome of the Fernandez-Moran type was used. In this microtome the specimen is mounted on a drum which rotates and is advanced by thermal expansion toward the diamond knife which is stationary so that one slice is cut per drum revolution. The slices were floated from the knife edge on a liquid bath usually containing water and a wetting agent. For convenience in handling, specimens were mounted in an araldite cold-setting resin. The slices were picked up on 200-mesh copper grids

(*a*) ×3000; illustrates uniformity of thickness obtainable over large area. Reduced one fourth in reproduction.

(*b*) ×80,000. Reduced one fourth in reproduction

FIG. 1.—Transmission Micrograph of Aluminum - 3 per cent Aluminum Oxide ("S.A.P.") Specimen Microtomed in the Cold Drawn Condition

for examination by transmission in a Siemens Elmiskop I electron microscope operated at 100 kv. A stereo specimen holder was employed so that specimens could be tilted critically to bring details into contrast.

TEST RESULTS

Copper-, nickel-, lead-, tin-, aluminum-, gold-, silver-, and platinum-base alloys have been successfully sectioned by the above technique, with the results described below.

Aluminum - Aluminum Oxide ("S.A.P."):

The specimen contained 3.0 per cent alumina and had been made from oxidized flake aluminum powder by hot extrusion of a hot-pressed compact followed by cold drawing to 86 per cent reduction. The wire, of 0.035 in. diameter, was cut transversely in the cold-worked condition.

Remarkably flat slices of uniform thickness were obtained as seen at low magnification (Fig. 1(*a*)). The long edge

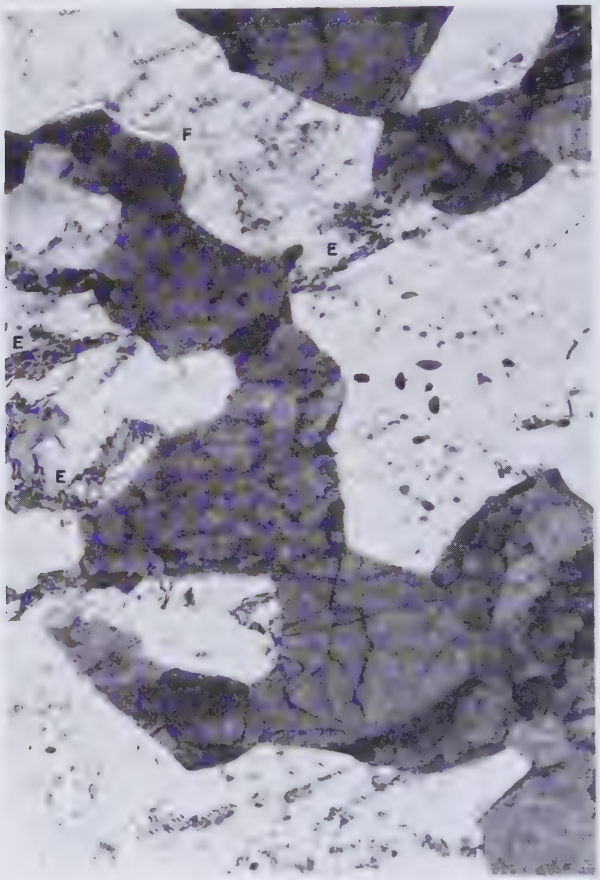


FIG. 2.—Transmission Micrograph of Aluminum - 40 Atomic per cent Zinc Wrought Alloy (×36,000). Reduced one third in reproduction.

of the slice is parallel to the cutting direction. Imperfections in the diamond cutting edge led to tool marks parallel to the cutting direction (Fig. 1(*a*)). The slices were probably only 100 to 200 Å thick and were readily penetrated by 40-kv electrons.

The alumina platelets gave rise to a mottled appearance at low power (Fig. 1(*a*)). The platelets were distinguishable from the aluminum matrix mainly by virtue of the fact that they diffracted more strongly and showed prominent tilt fringes visible at higher magnification (Fig. 1(*b*)). These indicate that most of the platelets are single crystals. Most of the platelets were 0.1 to 0.5 μ in diameter but a few were as small as 0.02 μ. The platelets appeared to be thicker than the foil. Dislocations may be seen apparently within the platelets as at *A*, appearing as black dots because they run nearly normal to the foil.

The surface was thinly coated with oxide which is occasionally visible as at *B* where it is rumpled and at *C* where it appears finely granular around a spherical inclusion of impurity.

The aluminum matrix subgrains extended through the thickness and were 0.1 to 0.5 μ in diameter. Dislocations were rarely observed within the subgrains but were sometimes resolved in subgrain boundaries. From the fact that microtoming introduces many dislocations in other metals, it would appear that nearly complete recovery had occurred in the 1-hr interval between microtoming and examination, the dislocations arranging themselves into low-angle grain boundaries. Some may also have escaped to sinks such as high-angle boundaries and the surfaces of the foil. Selected area electron diffraction gave ring patterns showing sharp spots supporting the view that recovery occurred.

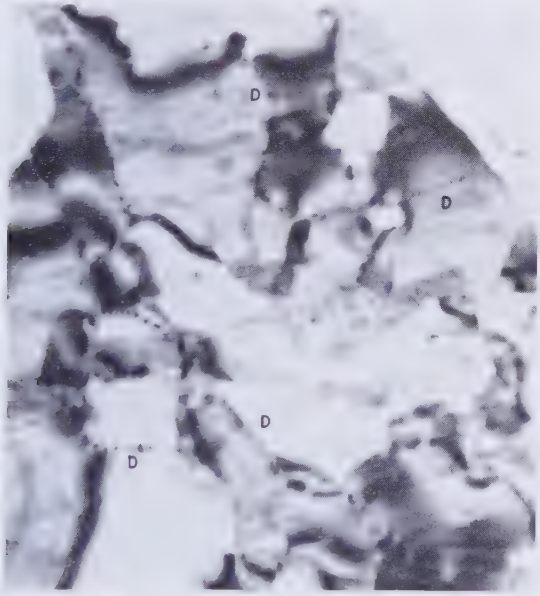


FIG. 3. Transmission Micrograph of Aluminum - 40 Atomic per cent Zinc Wrought Alloy Showing Structure in the Beta Phase (×100,000). Reduced one fourth in reproduction.

Recrystallization can be ruled out on the basis of the kinetics (8).

Aluminum - 40 Atomic Per Cent Zinc:

A high-purity aluminum - 40 atomic per cent zinc alloy was microtomed. The electron microstructure showed roughly equal amounts of light and dark areas (Fig. 2). The dark areas were apparently single phase, whereas the light regions usually contained small particles of dark phase. The light and dark phases were identified by selected area electron diffraction as being the aluminum-rich alpha and zinc-rich beta phases, respectively. The small particles of beta were probably precipitated from the alpha due to the decrease in the solubility of zinc in aluminum at low temperature. The marked contrast of the dark phase (Fig. 2) was apparently in part due to superficial oxidation of the specimen while floating on the water bath and was not tilt-sensitive.

FIG. 4.—Transmission Micrograph of Lead - 35 per cent Tin Cast Alloy (×55,000). Reduced one fourth in reproduction.

Well-formed subgrains of about 0.1 to 1 μ diameter were visible in the beta (dark) phase. Dislocations were resolvable in many of the sub-boundaries at higher magnification as at *D* in Fig. 3, and a few dislocations were sometimes

visible inside the subgrains. No extensive dislocation networks were seen in either phase. Small regions of network were occasionally seen in the light phase as at *E* in Fig. 2. It appears that recovery was practically completed in the hour or two between cutting and examination. The ease of recovery is indicated by the observation that subgrain growth could

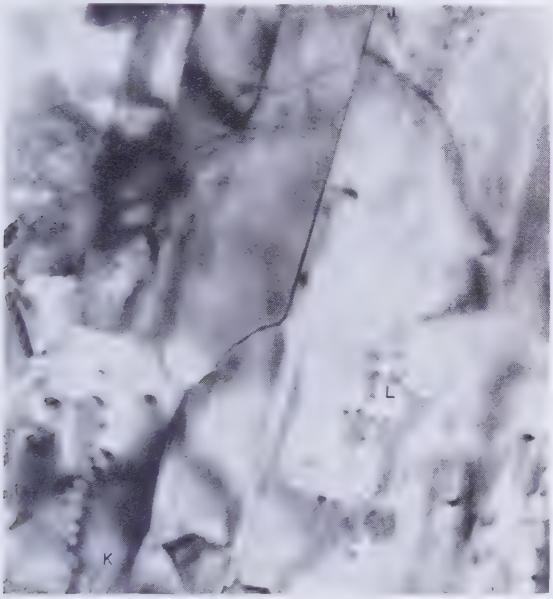


FIG. 5. Transmission Micrograph of Zinc Single Crystal Grown from the Melt (×140,000) Reduced one third in reproduction.

readily be produced in the beta (dark) phase by heating in the beam.

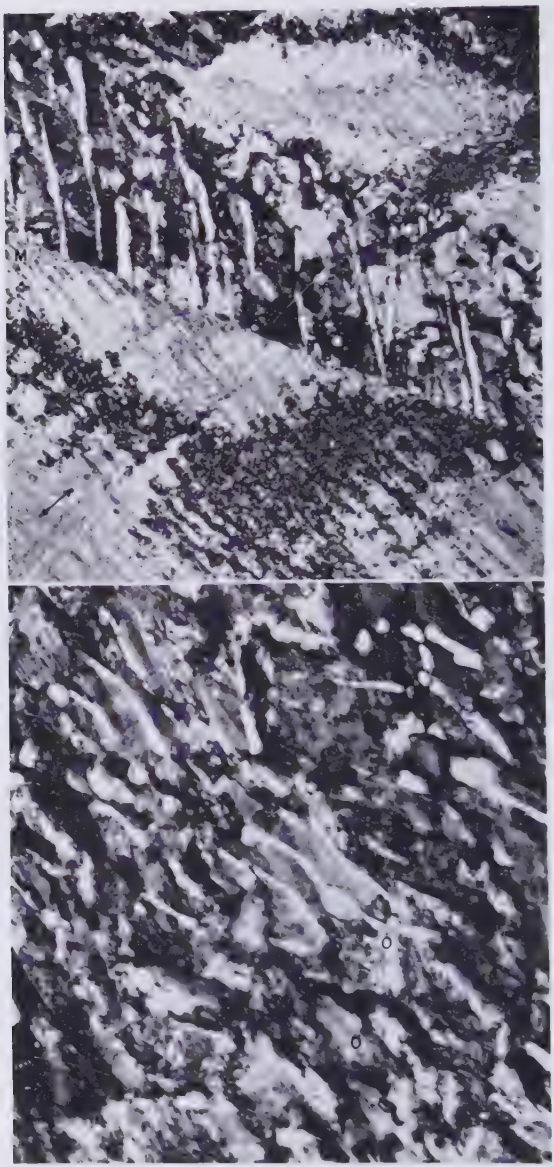
There was some tendency to crack along the phase boundary during microtoming as at *F* in Fig. 2. The structure is otherwise remarkably free from any macrodistortion associated with the cutting operation.

Lead - 35 Weight Per Cent Tin:

A high-purity lead alloy containing 35 per cent tin, sliced in the cast condition, showed dark and light phases (Fig. 4) which were identified by selected area diffraction as the lead-rich alpha phase and the tin-rich beta phase, respectively. The dark contrast of the alpha phase was not tilt-sensitive and was probably mainly due to surface oxide formed while the slices were floating on the water bath after cutting. This interpretation would account for the occasionally diffuse nature of the phase boundary and for the absence of contrast changes across subgrain boundaries within the alpha phase (Fig. 4).

It is clear from the phase diagram and the above information that the large dark area in Fig. 4 is a primary lead grain in which beta (tin) particles have been precipitated during cooling or subsequently and that the light area is a beta tin crystal presumably resulting from degenerate eutectic, the alpha phase of the eutectic separating on the preexisting primary alpha grain.

There appeared to be little or no shape



(*a*) Showing discontinuous precipitation at a grain boundary (×40,000). Reduced one third in reproduction.

(*b*) Fine structure in a region of discontinuous precipitation (×100,000). Reduced one third in reproduction.

FIG. 6.—Transmission Micrographs of Gold - 30 Atomic per cent Nickel Alloy Quenched and Aged to Cause Partial Transformation (×60,000). Reduced one third in reproduction.

distortion of the beta particles due to microtoming (Fig. 4). Since several apparently equiaxed particles of 500 Å diameter extended through the full thickness of the slice, the thickness is placed below 500 Å.

FIG. 7. Transmission Micrograph of Pure Silver (×140,000). Reduced one fourth in reproduction

Subgrains of about 0.1 to 0.7 μ diameter were observed in the beta phase and of about 0.05 to 0.4 μ diameter in the alpha phase. Individual dislocations were resolved in some sub-boundaries at higher magnification. Tangled dislocation networks were occasionally observed locally in both phases with densities of up to about 2×10^{11} per sq cm. The particles were often free from sub-boundaries, although particles *G*, *H*, and *I* in Fig. 4 contain boundaries. It seems clear that large numbers of dislocations are produced by microtoming, but that recovery is well

advanced within 2 hr of cutting when these micrographs were taken.

Zinc:

The structure of a crystal of 99.999 per cent purity zinc cut in the as-grown condition is shown in Fig. 5. A high-angle grain boundary *JK* is visible. Individual dislocations are visible as dots, for example at *L*. No regions of dense dislocation network were observed.

Certain regions had apparently recrystallized spontaneously between cutting and examination, others such as the one here had apparently recovered fairly completely. The differences are probably associated with local imperfections in the knife edge which lead to a greater or lesser degree of damage to the crystal slice.

Gold - 30 Atomic Per Cent Nickel:

Gold and nickel are completely miscible at high temperature but show a miscibility gap at low temperature. It is known (9) that the alloy may be quenched to retain a single phase and then aged to cause transformation by cellular precipitation into gold-rich and nickel-rich solid solutions.

Figure 6(*a*) shows a slice microtomed from the wrought alloy which had been heat treated to produce partial transformation. The structure is single phase except for the region of discontinuous precipitation on one side of the grain boundary *MN*. The continuous phase in the cellular precipitate is presumably the gold-rich phase. It appears that the nickel-rich phase nucleates at the grain boundary where it forms a chain of particles amounting to an almost continuous film and then grows into one grain. Figure 6(*b*) shows a region of discontinuous precipitation at higher magnification. In places, as at *O*, dislocation networks appear to be resolved with a mesh size of about 35 Å which for a foil thickness of 400 Å corresponds to a density of about 1.4×10^{12} per sq cm.

The cutting direction in Fig. 6(*a*) is indicated by the arrow. Faint lines are visible in the lower grain running nearly at right angles to the cutting direction. These are probably fault bands steeply inclined to the foil as described more fully in the next section. Their density is about 10^6 per cm. Their continuity indicates that there is no general precipitation within the grain.

Silver:

Polycrystalline silver rod of 99.99 per cent purity was annealed in vacuum for 1 hr at 300 C before cutting. The silver showed a single-phase structure (Fig. 7). Grain boundaries were visible (Fig. 7) but no dislocation structure was resolvable in them, indicating that they were high-angle boundaries. A damage track runs from *R* to *S* parallel to the cutting direction due to an imperfection on the knife edge. Deformation has evidently been more severe in this track, and is believed to be responsible for the jog at *T* in grain boundary *PTU*. Localized spontaneous recrystallization along the track appeared to be partially completed in the period of 2 or 3 hr between cutting and examination. Note, for example, the new grain boundary *RT*.

Individual dislocations running nearly normal to the foil were visible in some grains, for example in the region *V* (Fig. 7) in densities of about 3×10^{11} per sq cm. In other regions, for example at *W*, dislocations were arranged in fairly well-formed sub-boundaries.

In some regions dislocation movement could be produced using a localized electron beam of high intensity. Grain *UPQX* is of particular interest since dissociation of dislocations into Shockley partials connected by stacking fault was observed in it. For example, partials are visible at *Y* and *Z* connected by a fault

showing typical striped contrast. The dissociation width is about 700 Å, which is similar to the width observed in electron beam stressed silver films (10) and much greater than the calculated equilibrium separation. Another partial is visible at A, and it is clear that YZA may be regarded as part of a slip band in which a "train" of dissociated dislocations is moving along on the same plane or several "trains" on a set of parallel planes presumably of {111} type. This trast details along typical bands that these are fault bands rather than single stacking faults. The contrast arises at the intersection of the fault plane or planes in a fault band with the two foil surfaces. The bands are about 100 Å or less apart, corresponding to 10^6 bands per cm. A dislocation spacing of about 140 Å is observed in some of the bands in this grain. Assuming this spacing, the density of dislocations in this grain is about 7×10^{11} per sq cm.

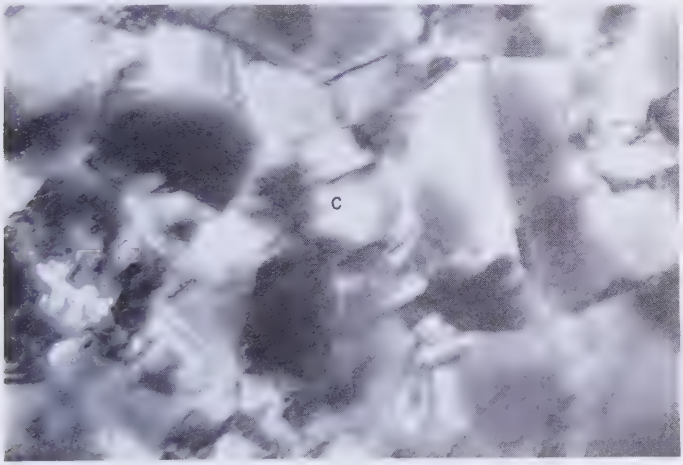


FIG. 8.—Transmission Micrograph of Pure Silver, Annealed After Microtoming (×100,000) Reduced one fourth in reproduction.

will be called a "fault band." It will be noticed that all of the faults in this grain have a common trace direction AV. Since it is not possible here to distinguish a fault intersection with the top surface from one with the bottom surface, the faults may be on one of two possible sets of {111} planes.

Large numbers of fault bands are seen in grain PQB. Due to the steep inclination of the active slip plane, typical stacking fault fringes are not visible, and the fault band typically shows a double line contrast. While a single widely extended fault could also show a double line contrast (11), it is clear from the con-

It was usually found that the fault bands run in a direction nearly transverse to the cutting direction. This may indicate that they form during the bending through 90 deg and straightening which occurs as the slice is cut vertically and transferred to the horizontal liquid surface next to the knife.

It is apparent from these observations that considerable deformation occurred during microtoming. Figure 8 shows the structure of a similar slice after annealing for 5 min at about 600 C *in vacuo*. Recrystallization has occurred to a considerable extent, giving grains 0.1 to 0.25 μ in diameter, some of which appear

to be relatively perfect. Regions of dense dislocation network are still present as at *C*. The local network mesh size is of the order of 100 Å, corresponding to a density of 10^{12} per sq cm.

Copper:

High-purity copper sheet containing 0.032 per cent oxygen, from a previous investigation (12), was annealed for 1 hr at 660 C in hydrogen. This treatment embrittled the material so that it broke readily on bending. The structure of the microtomed material is seen in Fig. 9, the direction of cutting being parallel to the damage tracks such as *DE*. A number of holes are visible, each presumably produced by reaction of an oxide particle with hydrogen. The holes show no sign of distortion due to the cutting operation and it would appear therefore that microtoming is ideally suitable for the preparation of specimens from bulk materials for the examination of fine porosity. Electrothinning would not be suitable for this purpose.

It is of passing interest to note that the holes tend to be faceted with 6 or more sides. The holes may assume the shape of the original cuprous oxide particles or, more probably, become somewhat enlarged as a result of the water vapor pressure built up inside them during annealing in hydrogen, so that the faceting may be related to the easy directions of plastic deformation of the surrounding crystal.

Dot-like contrast effects from dislocations nearly normal to the foil are visible in the vicinity of the extinction fringe *FG*. These are spaced about 500 Å, giving a local density figure of 4×10^{10} per sq

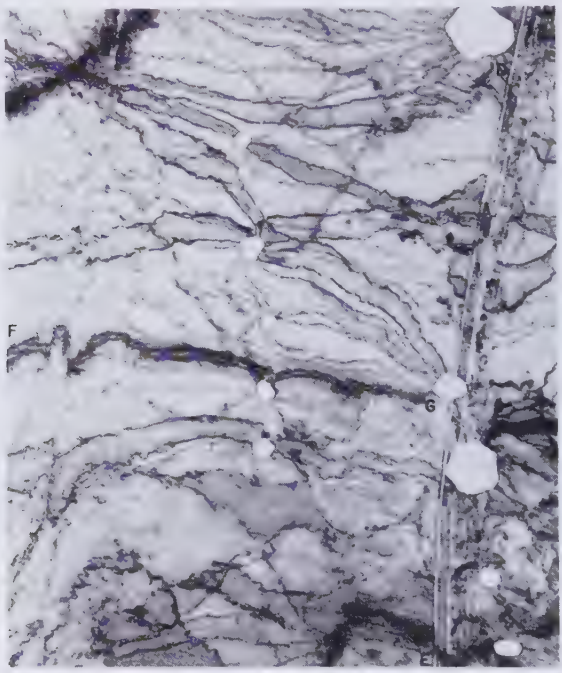
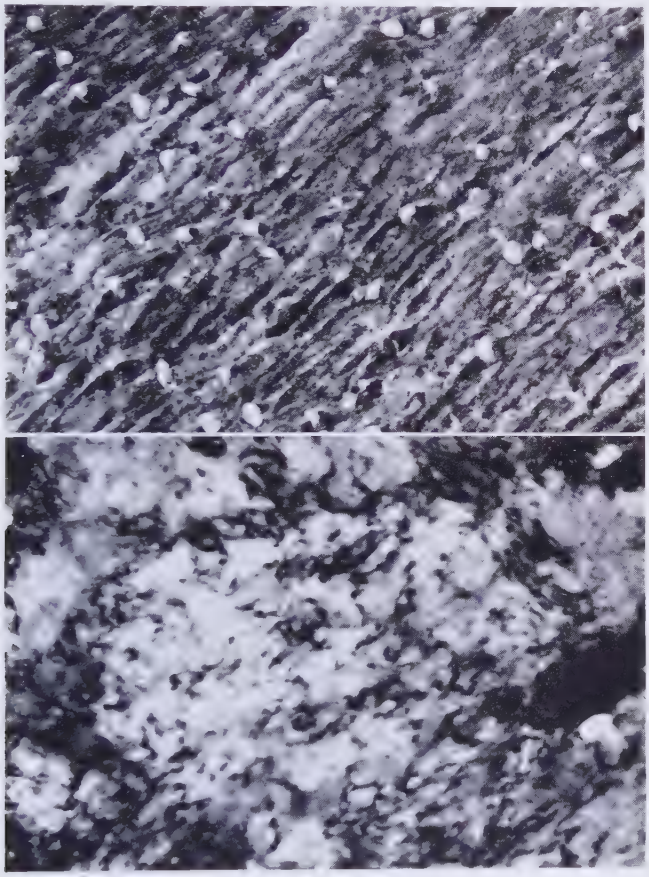


FIG. 9. - Transmission Micrograph of Oxygen-Bearing Copper, Hydrogen Annealed to Produce Cavities (×15,000). Reduced one third in reproduction.

cm. No evidence was seen of subgrain formation or of recrystallization which would be expected to occur at room temperature in severely deformed regions

fine wires in any desired direction. This copper-magnesium alloy wire specimen of 0.052-in. diameter had been completely oxidized internally in a copper-



(*a*) Showing particles (×40,000). Reduced one fourth in reproduction.
(*b*) Showing dislocations (×140,000). Reduced one fourth in reproduction

FIG. 10. Transmission Micrographs of Internally Oxidized Copper - 0.44 per cent Magnesium Alloy.

(12). It would appear therefore that there was little change in structure in the two hours between cutting and examination.

Internally Oxidized Copper - 0.44 Per Cent Magnesium:

Microtoming offers a unique method for preparing transmission specimens of

cuprous oxide-alumina pack at 900 C (13). After oxidation this alloy would be expected to contain about 1.8 volume per cent of magnesium oxide. The wire was microtomed transversely (Figs. 10(*a*) and (*b*)). Numerous roughly spherical particles, or holes where particles were, may be seen at low magnification fairly ran-

domly distributed in a single-phase matrix (Fig. 10(*a*)). The apparent particle size ranges from about 200 to 1100 Å, and the mean spacing is about 2000 Å, corresponding to a particle density of about 1.3×10^{14} per cu cm. The particles appear to be noncoherent. The slice thickness is estimated to be about 400 Å.

Dense networks of dislocations were commonly observed throughout the foils. most of the network is thought to form during microtoming.

Internally Oxidized Copper-0.20 Per Cent Aluminum:

This specimen is identical with the preceding one except for the composition. Randomly distributed equiaxed particles, presumably of alumina, were observed inside the grains. Extensive dislocation

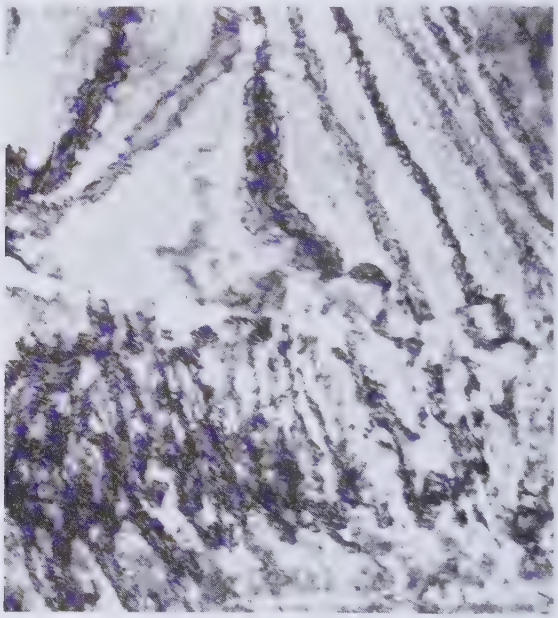


FIG. 11.—Transmission Micrograph of Internally Oxidized Copper - 0.20 per cent Aluminum Alloy Showing Particles at a Grain Boundary (×80,000). Reduced one fourth in reproduction.

Figure 10(*b*) shows an area of lower than typical dislocation density where the individual dislocations are more readily distinguishable. The density here is about 8×10^{10} per sq cm. Local densities of up to 5×10^{11} per sq cm were observed.

It is possible that dislocation networks begin to form near each particle during cooling after internal oxidation since the coefficient of expansion of magnesium oxide is somewhat smaller than that of copper, and local plastic deformation of the matrix would be expected. However networks were again present, presumably produced by microtoming. The particles appeared to be noncoherent. Chains of larger particles, or holes where particles were removed during cutting, were seen along grain boundaries (Fig. 11). These particles are no doubt mainly responsible for the loss of ductility in this material on internal oxidation (13).

Aluminum - 4 Per Cent Copper:

A high-purity wrought aluminum - 4 per cent copper alloy was solution treated

for 10 min at 520 C, water quenched, and aged for 5 hr at 160 C. This treatment would be expected (14) to precipitate G.P. [2] zones, otherwise known as θ'', which may be described as a coherent intermediate precipitate.

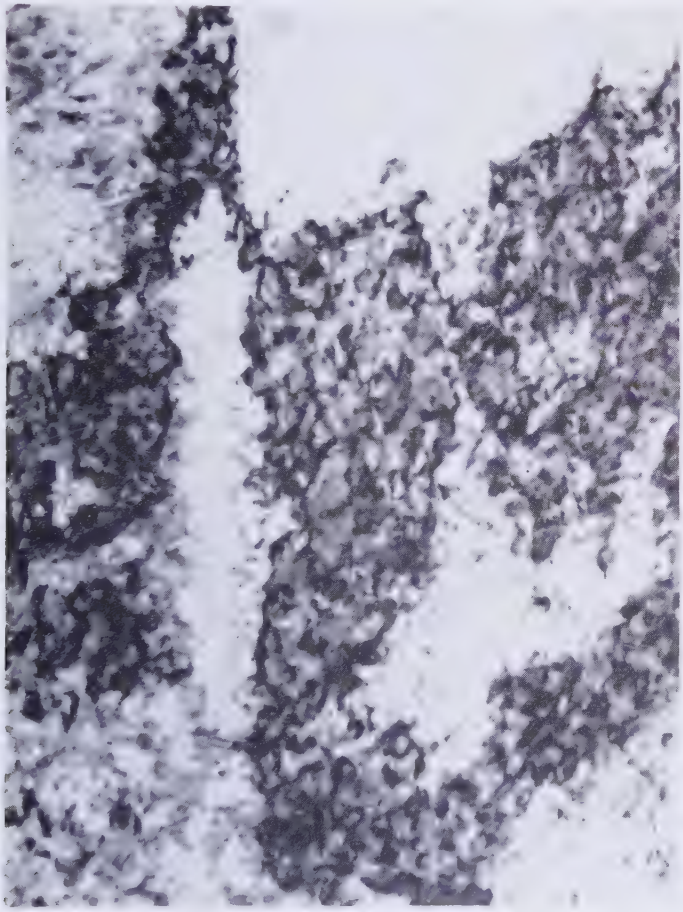


FIG. 12. Transmission Micrograph of Precipitation Hardened Aluminum 4 per cent Copper Alloy Showing GP[2] Zones and Associated Coherency Stains (×140,000). Reduced one fourth in reproduction.

The structure of the microtomed alloy consisted of plate- or rod-like precipitates in a single-phase matrix (Fig. 12). The precipitates were only clearly visible in the vicinity of extinction contours and appeared to be predominantly in one direction in a given area of a grain. The particles were 7 to 20 Å thick and 70 to 300 Å long. The density of particles is about 8×10^{16} per cu cm assuming a foil thickness of 400 Å. This is equivalent to a calculated mean spacing of about 230 Å for spherical particles. Selected area diffraction gave results compatible with the precipitates being θ'' as expected from previous work (14).

The contrast effects associated with the precipitate (Fig. 12) are very unusual.

It will be noticed that dark patches of contrast surround some precipitate particles and frequently overlap between a group of particles. Following previous work (14), this contrast is believed to originate in elastic coherency strains in the matrix around the particles. θ'' has a tetragonal structure which matches the aluminum unit cell in the *a* and *b* directions but is smaller in the *c* direction. The precipitate grows in such a way that elastic strains are minimized; that is, it assumes a platelike form with the *c* direction normal to the plane of the plate so that the matrix planes parallel to the plate are distorted. The structure observed (Fig. 12) corresponds to an aging stage near maximum hardness where the strain fields have become nearly continuous from one precipitate to the next.

The extensive coherency strain contrast made it difficult to identify dislocations positively except where they lay almost in the plane of the slice. Many of the dot-like features (Fig. 12) may be dislocations; however, no count is possible.

SUMMARY

Ultramicrotomy is shown to be a new and powerful technique for obtaining specimens of bulk metals and alloys for structure study by transmission electron microscopy. It is particularly valuable for studying the size, shape, and distribution of second-phase particles or holes. The method may readily be used in conjunction with selected area diffraction for phase identification. The method is not suitable for studying dislocations in bulk materials since microtoming itself introduces dislocation densities of up to about 10^{12} per sq cm. Coherency strains around second-phase particles are readily seen. Specimens of almost any initial shape may be cut.

Acknowledgment:

The author acknowledges the able assistance of J. A. Hugo in carrying out the experimental work.

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DIRECT TRANSMISSION ELECTRON MICROSCOPY OF ZIRCONIUM*

By A. P. Young,[1] C. W. Melton,[1] and C. M. Schwartz[1]

Although zirconium and titanium are hexagonal close-packed metals, the deformation mechanism is quite different in these metals from that in other hexagonal close-packed metals such as beryllium, zinc, and cadmium. Slip in zirconium and titanium occurs predominantly on prismatic $(10\bar{1}0)$ planes with possibly some slip on pyramidal $(10\bar{1}1)$ planes. Basal plane slip which predominates in the other hexagonal close-packed metals mentioned is observed rarely if at all in zirconium (1).[2]

One might expect that the dislocation arrays in both annealed and deformed zirconium and titanium would differ from those in metals where basal slip predominates. Specifically, stacking faults in the basal plane in zirconium and titanium would probably not be seen, since extended dislocations in the basal plane would tend to confine slip to basal planes. Churchman (2) has mentioned the possibility of extended dislocations in the prismatic plane to account for the fact that pyramidal $(10\bar{1}1)$ slip appears to be favored by increased interstitial content.

In this investigation, thin sections of zirconium and Zircaloy-2 were examined in the electron microscope. The purpose of the investigation was to relate the observed dislocation arrays and other structural features in the thin sections to the mode of deformation in zirconium.

Experimental Methods

Zirconium and Zircaloy-2 were thinned both chemically and electrolytically in nitric-hydrofluoric-lactic acid baths. In the electrolytic cell the hydrofluoric acid content was reduced until there was virtually no reaction with the zirconium at zero voltage. Metal removal occurred when the specimen was at the cathode. The reason for this apparent anomaly is obscure, but it probably means that metal removal was due only to chemical attack, while the somewhat reducing environment at the cathode prevented excessive oxide film formation and thus permitted chemical attack. Generally, the thin section surface was smoother with the electrolytic method. Surface quality depended on the history of the specimen from which the thin section was prepared. There was evidence that oxygen or nitrogen content of the metal was related to surface pitting.

Both foil and bulk specimens were used for preparing thin sections. Considerable difficulty was experienced with foil, in that the plane of the thin section as determined by selected area electron diffraction was invariably very close to the basal plane. For an adequate representation of dislocation arrays other orientations were desirable. Thin sections were made from platelets prepared from a forged zirconium ingot by sawing and grinding. Even in this instance there was

* Presented at a Technical Session June 26, 1961, during the Sixty-fourth Annual Meeting of the Society.

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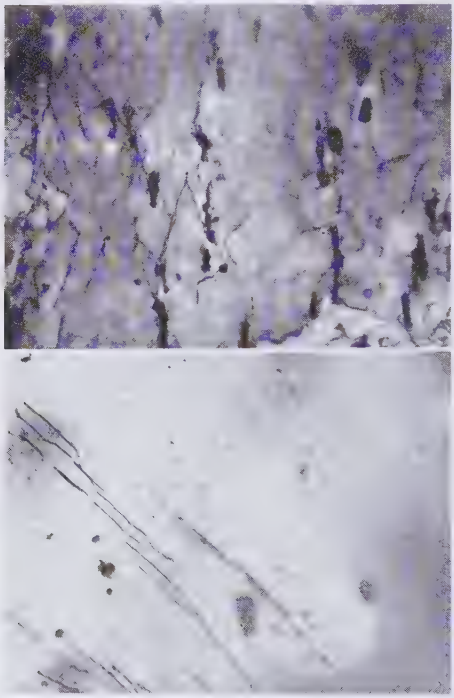
[2] The boldface numbers in parentheses refer to the list of references appended to this paper.

a preponderance of basal plane orientation. Finally, the orientation was randomized by heating zirconium foil into the beta phase field. A variety of orientations was obtained in thin sections prepared from beta annealed foil.



(*a*) Parallel to the basal plane (×20,000).
(*b*) Basal plane orientation (×40,000).

FIG. 1.—Zirconium Thin Section Prepared from an Ingot Plate That Was Annealed, Cold Reduced 10 per cent, and Reannealed.

RESULTS AND DISCUSSION

Extended dislocations may result in extended or contracted dislocation nodes (3). If extended dislocations occur in the basal plane in zirconium, interaction between $\langle 11\bar{2}0\rangle$ slip vectors of the type $[11\bar{2}0] + [\bar{2}110] \rightarrow [\bar{1}2\bar{1}0]$ should produce extended or contracted nodes. Nodes in the basal plane are shown in Fig. 1(*a*). None of them shows any perceptible extension or contraction.

In zirconium which has been worked and annealed, hexagonal dislocation networks could form on basal planes. Some intersections with angles close to 120 deg were seen as in Figs. 1(*a*) and (*b*). However, nothing that could be construed as networks was seen. It should be recalled that in metals such as iron (4) and stainless steel (3) where networks

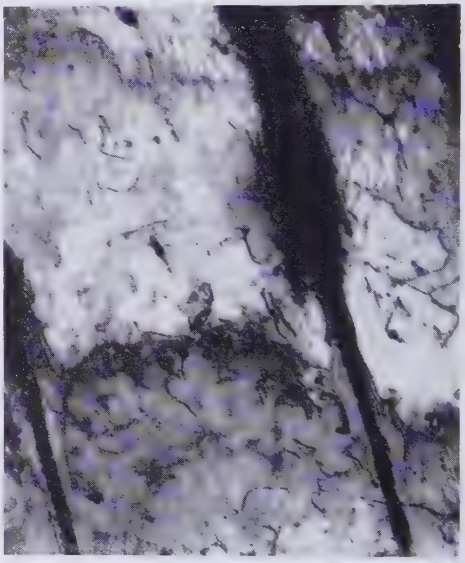


FIG. 2.—Zirconium Thin Section Prepared as in Fig. 1; Prismatic $(10\bar{1}0)$ Plane Orientation (×40,000).

have been observed, large areas have to be scanned to find them. Networks are present but not prevalent in metals, in contrast to such compounds as bismuth and antimony telluride (5) where networks are prevalent. The absence of networks in the zirconium thin sections examined does not mean they are never present. Not a great deal of thin area was suitable for observing dislocations. Most areas were either not thin enough or were marred by pitting or corrosion.

Figure 2 shows dislocations in a prismatic plane. Few nodes were observed in prismatic plane sections. Even though

extended dislocations in the prismatic plane were present as Churchman proposed (2), nodes would not be extended or contracted since only one of the interacting dislocations can be extended in a prismatic plane. If interactions occurred between partial dislocations in two or more nonparallel prismatic planes, they would be complex, as in the case of Lomer-Cottrell and stair-rod dislocations in face-centered cubic metals (3).

internal structure. This pitting may be related to oxygen pickup during the beta anneal. Precipitate was observed in many grain boundaries, as in Fig. 3(*b*). The precipitate may be related to segregation of oxygen to grain boundaries on cooling from the beta.

Thin sections of Zircaloy-2 were prepared from alpha annealed and cold rolled foil. No recognizable dislocations were observed in these heavily worked

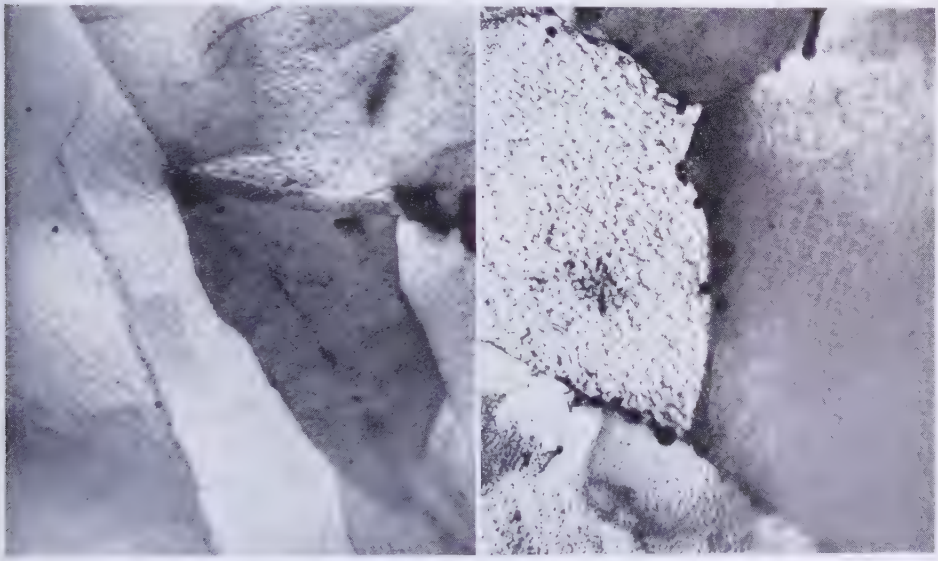
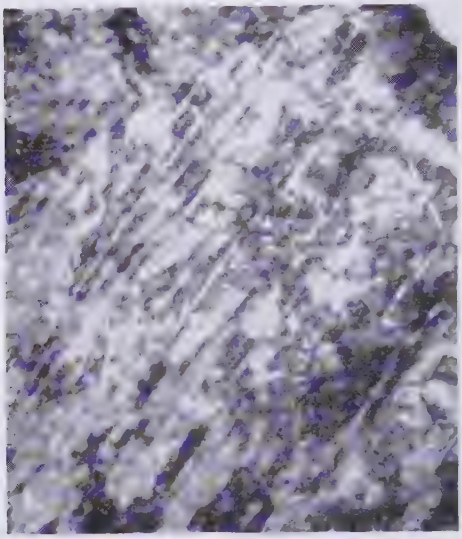


FIG. 3.—Zirconium Thin Sections Prepared from Beta Annealed Foil (×10,000).

The thin sections shown in Figs. 1 and 2 were prepared from zirconium ingot. In order to observe extended dislocations in the prismatic plane, either directly or by means of interactions with other dislocations, a variety of orientations in zirconium thin sections is necessary. It was found that annealing 1-mil foil above the alpha-beta transus randomized the orientation. Unfortunately, thin sections prepared from beta annealed material were not generally smooth, as seen in Fig. 3(*a*). Dislocations can be seen, but the pitting undoubtedly masks some

specimens. However, Zircaloy thin sections, prepared from foil annealed at 750 C and cold reduced about 10 per cent, exhibited arrays of parallel striations as in Fig. 4(*a*). Generally, at least two systems of striations were present. One system might be fragmentary as in Fig. 4(*a*). Figure 4(*b*) shows more detail in striations at higher magnification. Intersecting striations were always at an angle near 60 deg. The thin sections were close to the basal plane orientation. Thus, the striations could be parallel to prismatic planes, which are the most



(*a*) ×25,000.

(*b*) ×100,000.

FIG. 4.—Zircaloy-2 Thin Section Prepared from Foil Annealed at 750 C and Cold Reduced 1 per cent.

active slip planes in Zircaloy. It is likely that some slip occurs on all the slip systems during rolling; therefore, the striations may be traces of slip that occurred during rolling.

The lack of offset, and the fact that striations are not always continuous across intersections, as seen in Fig. 7, indicate that slip on one set of planes in zirconium may block slip on a second set. Blocking of slip on intersecting slip bands may occur in some other metals and has definitely been observed in lithium fluoride crystals (6). Blocking should be possible only when dislocations moving on a slip plane leave in their wake a trail of dislocations or other defects. The nature of these trails has been related by Gilman and Johnston (7) to the cross-glide multiplication mechanism for slip-band formation originally proposed by Koehler (8). In comparing lithium fluoride and zirconium it is interesting to note that they are similar to the extent that cross-glide planes are not planes of easy slip in either material. This is in contrast to face-centered cubic and body-centered cubic metals in which cross-glide planes are planes of easy slip. In zirconium the cross-glide planes are pyramidal, and primary slip in zirconium occurs rarely if at all on pyramidal planes (1).

Formation of new loops on cross-glide planes near a primary slip plane is incidental to dislocation multiplication. In face-centered cubic and body-centered cubic metals, the trailing loops in cross-glide planes may be dispersed over a broad band and would not constitute as effective a barrier to duplex slip as in Zircaloy or lithium fluoride where the trailing loops are probably closer to the primary slip plane and concentrated in a narrower band. If the striations in Fig. 4(*b*) are due to etching out along slip planes, the indication is that the band of high dislocation density is only a few lattice spacings wide.

SUMMARY

Zirconium and titanium have deformation modes different from other common metals and are therefore of interest for thin film observation. For a more definitive analysis of dislocation arrays in zirconium, an improvement over the present thinning technique is needed to give consistently smooth thin sections. Also, control over interstitial content during beta anneal would be desirable since the use of annealed and deformed beta annealed foil appears to give the most random orientation.

For disclosing slip line traces, an alloy may be preferable since preferential etching at dislocations is generally dependent on the presence of an impurity.

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IFFUSION MEASUREMENTS IN IRON-NICKEL WITH THE ELECTRON PROBE MICROANALYZER*

By S. Ohh[1] and K. G. Carroll[2]

When nickel-plated steel is heated to temperatures required for hot rolling, the familiar "alloy layer" zone is observed in the microstructure. Preliminary observations in the Castaing electron probe microanalyzer showed that this zone is merely a region of solid solution in which composition varies widely. No obvious meaning can be attached to the composition limits of the iron-rich and nickel-rich sides of this zone. A systematic investigation has been carried out to study the interdiffusion of the two metals.

Experimental Procedure

Nickel was plated from an ordinary Watts-type solution upon specimens of AISI 1010 steel. Diffusion anneals were made by encapsulating small specimens in evacuated quartz tubes prior to heating in the furnace. Diffusion couple specimens were cut parallel to the direction of diffusion, metallographically polished, and measured (unetched) in the electron probe instrument. An electron accelerating voltage of 24 kv was used, with a beam current of 2×10^{-8} amp electronically regulated for stability. Under the conditions of measurement, accurate data on local chemical composition were obtainable on the micron scale. By the use of homogeneous standards of known compositions, small corrections were applied to the observations to eliminate absorption and fluorescence effects. The data so obtained were analyzed in terms of the well-known solutions to Fick's equation under appropriate boundary conditions. Temperatures of 1800, 2010, and 2280 F were employed; all diffusion occurred in the austenitic phase of steel.

Experimental Results

Figure 1 is a typical plot of the data, on arithmetic probability paper, showing the iron distribution in the specimen diffused for 2 hr at 2280 F. The linearity of the curve indicates that Fick's equation with a constant diffusion coefficient, D, is well obeyed here for iron concentrations up to 70 per cent. Similar plots well represent the data obtained at the lower temperatures. From these curves the slope of the straight line is $\frac{1}{2}\ (Dt)^{1/2}$ and the diffusion coefficient is obtained directly (1).[3]

Diffusion coefficients obtained at three temperatures are shown in the Arrhenius plot of Fig. 2. These measurements give the following values of the activation energy Q and frequency factor D_0 :

Q = 43 kcal per mole, and
$D_0 = 1.9 \times 10^{-3}$ cm² per sec.

Figure 3 compares the measured data

* Presented at a Technical Session during the Sixty-third Annual Meeting of the Society, June, 1960.

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[3] The boldface numbers in parentheses refer to the list of references appended to this paper.

with the solution of Fick's equation based upon the measured diffusion coefficient, for a couple diffused at 2280 F for 2 hr. These measurements pertain to the nearly ideal case of one-dimensional diffusion in media of infinite extent.

For long diffusion times or very thin nickel coatings, the problem becomes that of diffusion in a semi-infinite medium. Initial conditions become, for a plating thickness h,

$$C = Co \text{ for } 0 < x < h$$
$$C = 0 \text{ for } x > h$$

The solution (see, for example, reference (2)) is then expressed as the sum of two error functions:

$$C = \frac{Co}{2}\left[\operatorname{erf}\left(\frac{h+x}{2\sqrt{Dt}}\right) + \operatorname{erf}\left(\frac{h-x}{2\sqrt{Dt}}\right)\right] \quad (1)$$

At the outer surface of the couple ($x = 0$) this reduces to

$$C_{x=0} = Co \operatorname{erf}\left(\frac{h}{2\sqrt{Dt}}\right) \quad (2)$$

This equation may be used to simplify the procedure for measuring diffusion coefficient, D, by requiring accurate measurement only of the surface concentration, initial thickness of nickel layer, h, and the time of diffusion, t. Coefficients so measured are found to be consistent with those given above for the case of infinite solids. It should be noted that the small penetration, here about 1 μ, of the electron probe is necessary for using this simplified procedure to measure diffusion coefficients.

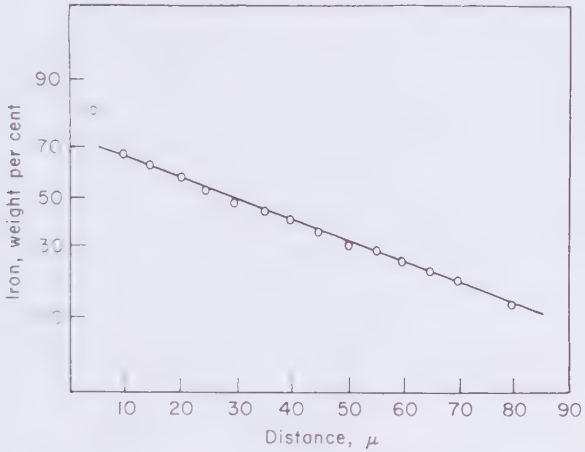


FIG. 1.—Probability Plot of Iron-Nickel Diffusion at 2280 F for 2 hr.

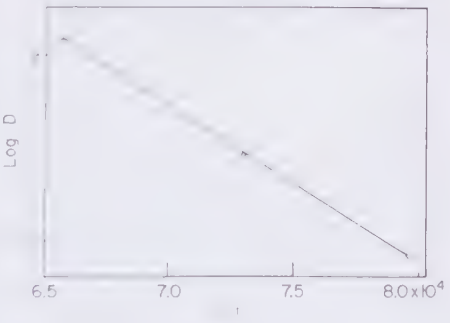


FIG. 2. Log D Versus $1/T$ Plot.

DISCUSSION

It has been frequently pointed out that diffusion constants D_0 and Q measured in polycrystalline metals are subject to considerable uncertainty because of the well-known difficulties of separating grain

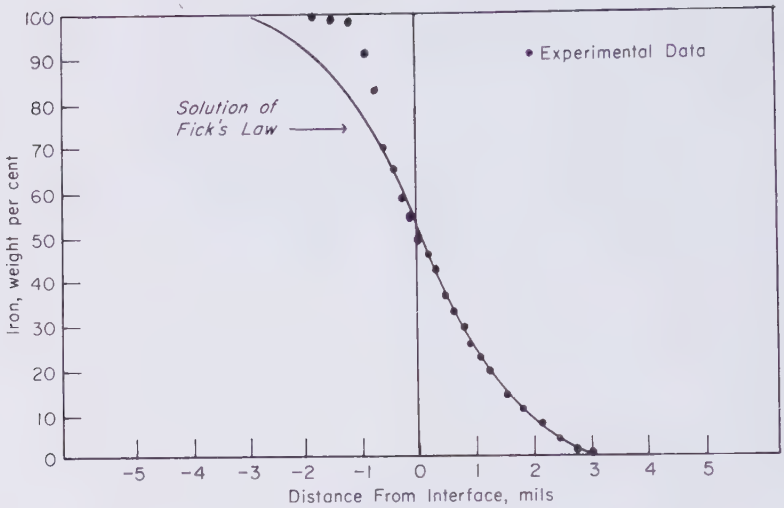
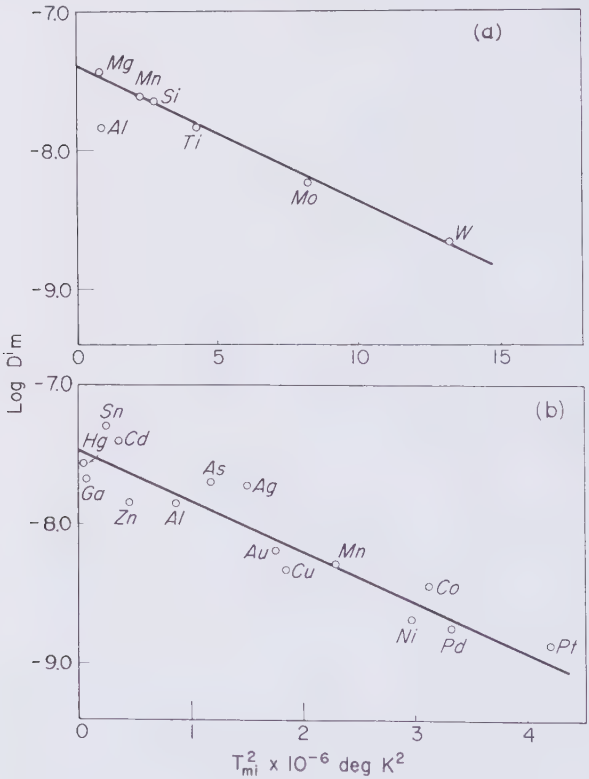


FIG. 3.—Concentration-Penetration Curve After 2 hr at 2280 F.



(*a*) In nickel.
(*b*) In copper.

FIG. 4.—Correlation of Log D_m^i Versus T_{mi}^2 in Nickel and Copper.

boundary and lattice diffusion. Zener's expression (3) for D_0 is as follows:

$$D_0 = \gamma a^2 \nu e^{\Delta S / R}$$

where:

γ = a numerical constant, nearly 1 for face-centered cubic lattices,
a = the lattice parameter,
ν = the vibrational frequency of an atom in its equilibrium position,
R = the gas constant, and
ΔS = the entropy change associated with the diffusion process.

If one substitutes the above measured value of $D_0 = 1.9 \times 10^{-3}$ cm² per sec along with appropriate constants, the entropy change ΔS comes out negative, a physically inadmissible situation.

Nowick (4) has shown that there is a systematic lowering of measured values of D_0 and Q by grain boundary diffusion. He suggested that the most reliable value to be obtained from experiment is that measured as close as possible to the melting temperature, subsequently corrected by knowledge of the temperature coefficient of elastic modulus. If the measured values here are thus corrected, using Nowick's Eq 5 (reference (4)) the values obtained are:

Q = 66 kcal per mole, and
D_0 = 3.4 cm² per sec.

These constants are appropriate to pure lattice diffusion in the iron-nickel system, and are consistent with theoretical interpretations of the vacancy mechanism of diffusion.

If literature values of diffusivity (4-6) in dilute solutions are extrapolated to the melting temperature of the solvent, a wide variety of data may be correlated (7). By plotting the diffusion coefficient of the solute at the melting point of the solvent, D_m^i, as a function of the square of the melting temperature of the solute, a linear curve approximates the data. Figures 4(*a*) and (*b*) show this correlation for solute additions to nickel and copper. Figure 4(*b*) includes the semi-empirical values of Nowick (4). The lines drawn may be fitted to the equation:

$$D_m{}^i = \gamma_0 \exp(-\alpha T_{mi}{}^2)$$

with:

α = 8.3×10^{-7} deg K^{-2} for copper,
2.2×10^{-7} deg K^{-2} for nickel, and
γ_0 = 3.8×10^{-8} (± 0.3) cm² per sec for both copper and nickel.

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THE DEVELOPMENT OF ELECTRON MICROSCOPIC METHODS FOR THE STUDY OF METALS

By W. C. Bigelow[1]

Although the first electron microscopes were built in the early 1930's, electron microscopy did not become established as a widely used experimental method until after 1945 when reliable, refined commercial instruments became generally available. During the period from about 1945 to 1955, biological applications of electron microscopy greatly outnumbered nonbiological applications and exerted a dominating influence on developments in instrumentation and techniques. During the past few years, however, there has been a tremendous increase in the use of electron microscopy in nonbiological areas, and especially in metallurgy. This recent trend has begun to exert a strong influence on the general course of developments in the field of electron microscopy and is contributing much new and valuable information about the structures of metals. Subcommittee XI on Electron Microstructural Studies of Metals (of ASTM Committee E-4 on Metallography) has contributed actively to this progress in nonbiological applications of electron microscopy through its program of work on the development of techniques for electron microscopic studies of metals (**1**–**8**).[2]

The purpose of this article is to describe some of the important developments in instrumentation, techniques, and applications that have accompanied this growth of electron metallography. The first part of this article deals with developments relating to the use of the common transmission type of electron microscope in metallurgical work, while the second part describes the development of reflection, scanning, mirror, emission, and point-projection microscopes, which are less commonly used but which are particularly well suited for direct observation of the surfaces of metallurgical specimens.

Development of Transmission Microscopy

Instrument Design:

While electron microscopes have been improving continuously since the first ones were built in the 1930's, recent progress has been particularly rapid and impressive. The principal emphasis in the past has been on improving the electron optical systems to achieve better resolution, higher magnification, and greater versatility of optical performance. Recently, however, considerable attention has also been given to revising the general design and construction of the microscopes to provide greater convenience of operation and maintenance and to permit the use of special attachments for treating the specimen in various ways while it is under observation in the microscope (**9**).

At present, more than a dozen different models of electron microscope

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[2] The boldface numbers in parentheses refer to the list of references appended to this paper.

TABLE I.—CHARACTERISTICS OF ELECTRON MICROSCOPES

NOTE.—The information in this table may not be accurate or up-to-date because of the rapidity with which changes in design are being introduced and the difficulties in compiling data of this type.

Manufacturer	Model	Accelerating Voltage, kv	Resolving Power, A	Electronic Magnification	Lens System[a]	Photographic Exposures and Plate Size	Special Features[b]
Bendix Aviation Corp. (Akashi)	TRS-80	50, 80	12	1500 to 80,000×	O, I, P	24—65 by 90 mm, (F[b])[c]	S, (St, TR, H, C)[c]
Hitachi Ltd. (U.S. Dealer: Erb and Gray Scientific)	HU-11A	50, 75, 100	7	200 to 250,000×	DC, O, I, P_i	18—3¼ by 4 in.	S, (St, TR(H), RM, T, H, C, X, G)[c]
	HS-7	50	12	1500 to 50,000×	C_p, O_p, I, P_{pr}	18—3¼ by 4 in.	
	HS-6	50	15	2000 to 30,000×	C_p, O_p, I_p, P_p	18—3¼ by 4 in.	S, TR, (X)[c]
Japan Electron Optics Laboratory Co., Ltd. (U.S. Dealer: Fisher Scientific Co.)	JEM150	80, 100, 150	10	600 to 200,000×	DC, O, I, P	24—54 by 70 mm	S, (TR, H, C, T, G, M)[c]
	JEM-6A	50, 80, 100	8 to 12	600 to 200,000×	DC, O, I, P	24—65 by 90 mm	S, (ST, TR, RM(H), T, H, C, X, G(H), M)[c]
	JEM-6C	50, 80, 100	8	600 to 200,000×	DC, O, I, P	24—65 by 90 mm	S, (ST, C)[c]
	JEM-T6	60	20	500 to 30,000×	C, O, I, P	24—65 by 90 mm	S, TR
	JEM-T1	50	50	2500 to 5000×	O, P	2—54 by 70 mm	
	EM-200	40, 60, 80, 100	10	250 to 200,000×	DC, O, DI, P	12—3¼ by 4 in., F[b]	S, St, TR, (T, H, C)[c]
Philips Electronics Inc.	EM-100B	40, 60, 80, 100	15	300 to 100, 000×	C, O, DI, P	F (5—3¼ by 4 in.)[c]	S, St, (TR, T, H)[c]
	EM-75B	0 to 75	30	300 to 12,000×	C, O, P	F (8—2 by 2 in.)[c]	St, (T, X)[c]
Radio Corp. of America	EMU-3G	50, 100	10	700 to 50,000× (200,000×)[c]	C, O, I, P, (DC)[c]	5—2 by 2 in., (F[b])[c] 3—3¼ by 4 in.	S, St, (TR(H), H, C, T)[c]
Siemens and Halske (U.S. Dealer: Siemens New York Inc.)	Elmiskop I	40, 60, 80, 100	10	210 to 200,000×	DC, O, I, P_r	12—65 by 90 mm, (F[b])[c]	S, St, Si (TR(H), C, T)[c]
Carl Zeiss (U.S. Dealer: Carl Zeiss, N. Y.)	EM-9	60	10 to 20	1500 to 35,000×	O, I, P	20—70 by 70 mm	S, St
Associated Electrical Industries (U.S. Dealer: Picker X-Ray Corp.)	EM-6	50, 75, 100 (25 to 50)[c]	8 to 15	1500 to 120,000×	DC, O, I, P	6—3¼ by 4 in., (F 70)[c]	S, St (TR, RM, T, H, C, G)[c]
Mikros Inc.	EM-20	10 to 40	25 to 35	1000 to 20,000×	C_e, O_e, I_e, P_e	5—2 by 2 in., F	S, St

[a] C = condenser, O = objective, I = intermediate, P = projector, D = double, r = multiple pole pieces on rotating stage interchangeable during observation, p = permanent magnet lens, and e = electrostatic lens.

[b] S = selected area diffraction, St = stereomicroscopy, TR = transmission reflection diffraction stage, RM = attachment for reflection microscopy, T = specimen holder for tensile deformation of specimens, H = specimen heater, C = specimen cooling device, X = attachment for X-ray projection microscopy, G = goniometer for tilting specimens, M = camera attachment for recording moving pictures directly on movie film, Si = simultaneous diffraction from two specimens, F = camera for 35 mm film, and F 70 = camera for 70-mm film.

[c] Accessories available at extra cost.

manufactured by nearly as many different companies are being marketed in the United States. Selected characteristics of several of these instruments are summarized in Table I to show how extensively the various developments discussed below have been incorporated into present commercial instruments. While the information given in this table has been reviewed recently by representatives of the respective manufacturers, it may not be complete or up-to-date in all cases due to the rapidity with which changes in design are being introduced and to the difficulties involved in categorizing features of such complex and diversified instruments. It should also be emphasized that the data in this table are not intended to provide an adequate basis for making a choice in the purchase of an electron microscope, for it has been necessary to omit from the table many important features that should be given careful consideration in this connection.

The present commercial instruments may be divided into two broad, and somewhat overlapping, classes. First there are the de luxe "universal" microscopes designed to give the highest possible resolution and magnification and to include as many as possible of the recent refinements in instrumentation and design. These are recommended for applications where excellence and versatility of performance are primary requirements. Two instruments of this type, the RCA Model EMU-3G and the Hitachi Model HU-11, are shown in Figs. 1 and 2. Second, there are the less elaborate, and also less expensive "utility" instruments such as the Philips EM-75 shown in Fig. 3 which usually provide slightly lower resolving power and magnification and are more limited in performance than the "universal" microscopes. These instruments are capable of high-quality work, however (as demonstrated by the micrographs of stacking faults and oxide nuclei in Figs. 19 and 24 which were taken with a Philips EM-75 microscope), and should be of particular interest to metallurgists since they provide all features needed for routine examination of metallurgical specimens by replica techniques. Their relatively low cost makes them especially attractive for inspection and process control work. Instruments of even more simplified design for controlling specimen preparation and other routine operations are being developed (10,11).

The guaranteed resolving power for most present electron microscopes is from 2 to 5 times better than the 50 Å value which prevailed for most of the better microscopes of about 10 years ago (12). A major part of this substantial increase in resolving power has been achieved by incorporating devices known as "stigmators" or "compensators" into the objective lenses of the instruments to correct for astigmatism caused by asymmetries in the lens field. Although these devices were first described as early as 1947 (13), it was some time later before they became widely adopted as a basic feature of the objective lens. In addition, fundamental studies of electron optics have led to improved lens designs which minimize image distortion, diffraction effects, and chromatic and spherical aberrations. More effective use has been made of magnetic shielding to eliminate image distortions due to stray internal and external magnetic fields. The stability of electrical circuits has been improved greatly, reducing image movement due to fluctuations in lens currents and electron-accelerating voltage. Image movement due to mechanical vibrations has also been reduced to an extremely low value through greatly improved structural designs.

Two interesting examples of high-resolution microscopy are shown in

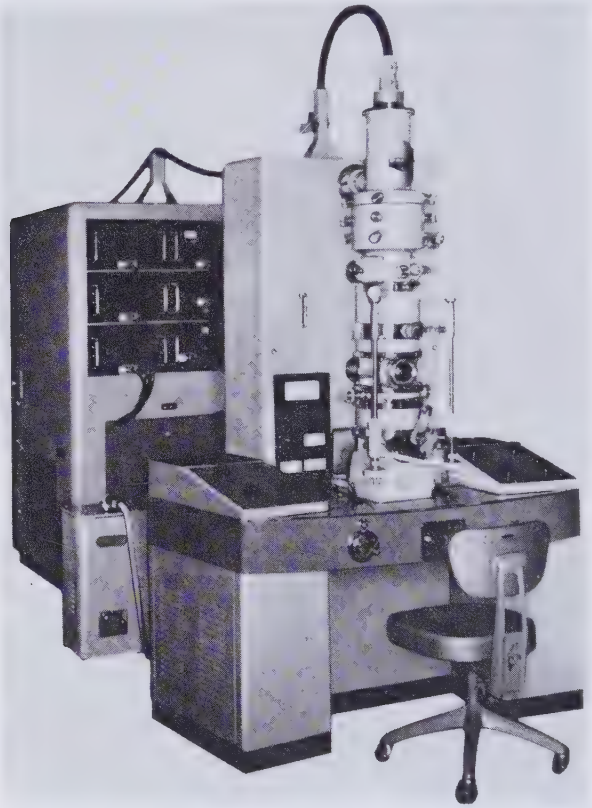
Figs. 4 and 5. The micrograph in Fig. 4 shows clearly resolved fragments of deoxyribose nucleic acid molecules having an average diameter of about 20 Å (14). Figure 5 is a micrograph of a thin crystal of potassium chloroplatinite, showing the resolution of individual lattice planes separated by about 7 Å (15). Haine and Mulvey (16) have achieved 5 Å resolution in very carefully controlled experiments, closely approaching the theoretical limit of about 3 Å for present types of instruments (17). This limit results from spherical aberration which is inherent in the type of lenses used (18), although the present inability to achieve this limit appears to be due to such factors as specimen contamination and image movement caused by mechanical, thermal, and electrical instabilities. The possibility of exceeding this limit by elimination of spherical aberration through the use of new types of lenses is being actively investigated (19–21) in the hope of approaching resolving powers

Courtesy ... Review ... of ... American ...

FIG. 1. RCA Model EMU 3G Electron Microscope.

in the range of $\frac{1}{20}$ to $\frac{1}{30}$ Å such as would be expected if resolution were controlled only by diffraction effects dependent on the wavelengths of the electrons.

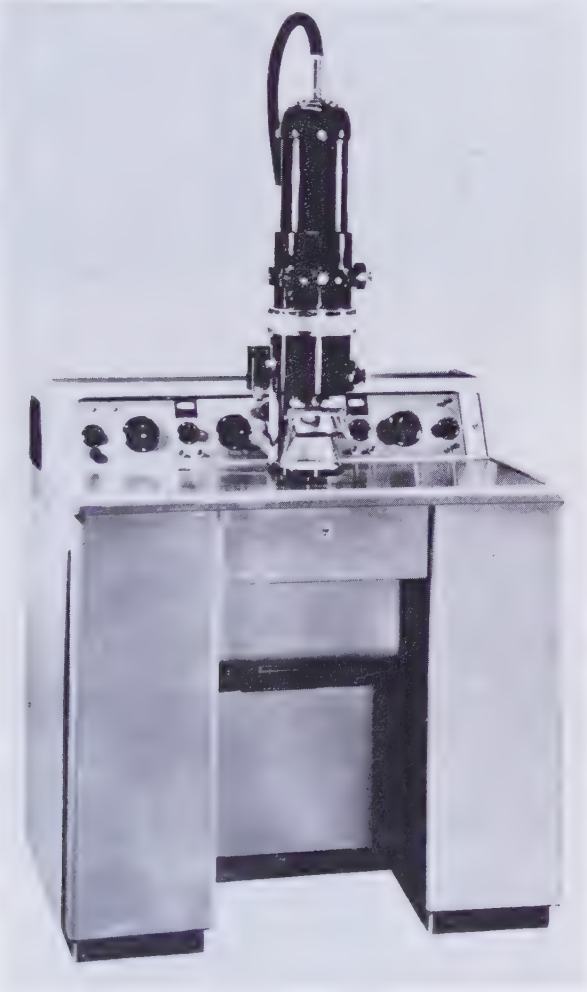
The magnifications attainable with the newer electron microscopes are also substantially greater than those attainable with previous models. This increase in magnification has been achieved mainly by increasing the number of lenses in the electron optical system. Early electron microscopes which were designed primarily by analogy with optical microscopes (22) employed only three lenses: a condenser lens for controlling the illumination of the specimen, an objective lens for producing the first magnified image, and a projector lens (corresponding to the ocular of the optical microscope) which provided a second stage of image magnification and produced the final image which was observed on the fluorescent screen or recorded photographically. With these instruments the normal range of magnification was from about 200× to about 20,000×, and in many cases it was necessary to dismantle the optical column partially and change pole pieces in the projector or the objective lenses, or both, to cover this range entirely. Following the design introduced by Phillips (23,24) and Metropolitan-Vickers (25), nearly all recent models



Courtesy of Erb and Gray Scientific, Inc.

FIG. 2.—Hitachi Model HU-11 Electron Microscope.

have an "intermediate" lens located between the objective and projector lens, as shown in Fig. 6, to provide a third stage of magnification. With this arrangement, magnifications ranging from less than 1000× to more than 200,000× can be obtained by adjustment of lens currents only, and the image can be kept in observation as the magnification is varied over this entire range. These high levels of direct magnification are important in high-resolution work for they permit the electron image to be recorded with sufficient enlargement to prevent fine details from being obscured by the inherent graininess of the photographic plates. Since the image can be further enlarged as much as ten times in the photographic printing process without loss of resolution, total useful

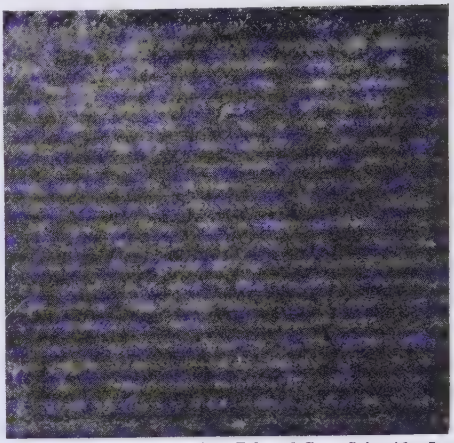


Courtesy of Philips Electronics, Inc.

FIG. 3. Philips Model EM-75 Electron Microscope.

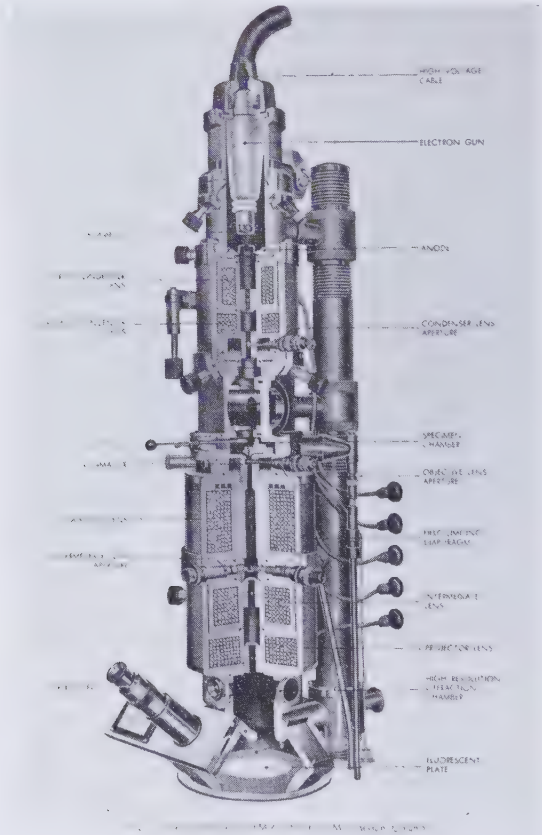
Courtesy of C. E. Hall, Department of Biology, Massachusetts Inst. Technology.

FIG. 4.—Segments of Linear Molecules of Deoxyribose Nucleic Acid Approximately 20 Å in Diameter (× 60,000).



Courtesy of D. Evins, Erb and Gray Scientific, Inc.

FIG. 5.—Potassium Chloroplatinite Crystal Showing Resolution of Lattice Planes Separated by 6.99 Å (× 4,300,000).



Courtesy of Japan Electron Optics Laboratory Co., Ltd.

FIG. 6.—Cross-Section of the Column of the JEM-6A Electron Microscope.

magnifications in excess of one million fold can be obtained. Work over a range of magnifications is further facilitated in most recent models of electron microscopes by optical systems designed so that the wide-angle distortions of the intermediate and projector lenses virtually cancel one another, thus eliminating distortion over wide areas in the final image and permitting photographic plates as large as $3\frac{1}{4}$ by 4 in. to be used in recording the micrographs (26). This is advantageous in metallurgical studies at all magnifications for it allows larger and more representative portions of the microstructure to be included in a single micrograph without distortion.

In addition to contributing to the attainment of high magnification, the intermediate lens plays an important role in the selected area diffraction feature of the modern three-stage electron microscopes. In obtaining a selected area diffraction pattern, the strength of the intermediate lens is adjusted so that the back-focal plane, rather than the image plane, of the objective lens is focused onto the object plane of the projector lens. This causes the electron diffraction pattern produced by the specimen, rather than the electron optical image of the specimen, to be displayed on the viewing screen. Most modern microscopes have provisions for rapidly adjusting the strength of the intermediate lens to the value required for viewing the diffraction pattern and are equipped with an adjustable field-limiting aperture which can be inserted into the image plane of the projector lens. With this arrangement it is possible, while observing a specimen, to outline a selected area of it with the diffraction aperture, and immediately obtain a diffraction pattern from the material in that area. This provides a very effective method for identifying selected particles of crystalline materials that is finding extensive use in studies of precipitates of alloy systems.

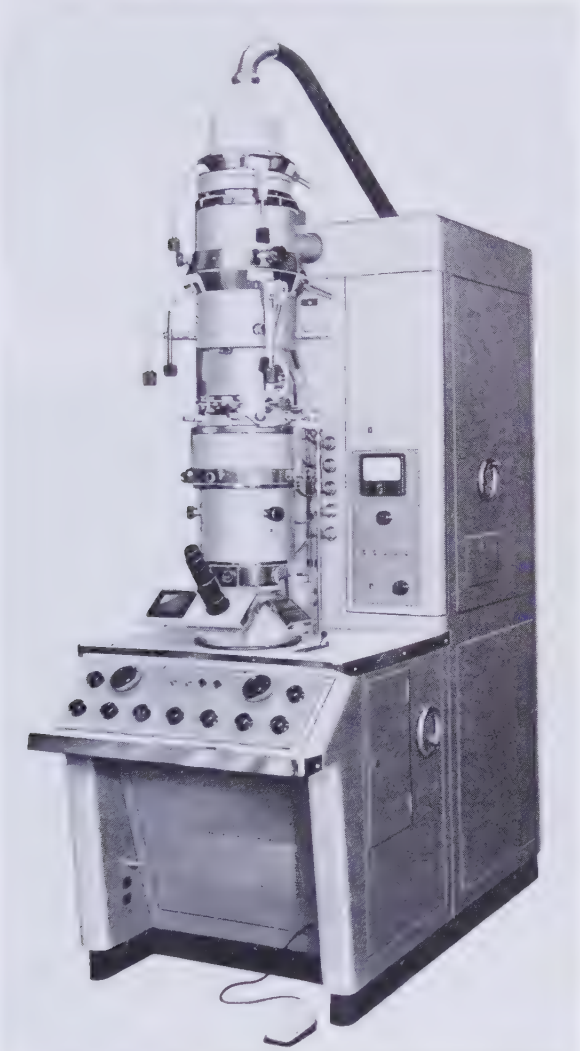
In addition to the intermediate lens, other lens elements have been added to the basic three-lens optical system. For example, some models of the JEM-5 microscopes employed a two-stage objective lens; the Philips EM-100 and EM-200 microscopes both contain a second intermediate or "diffraction" lens; while the Siemens Elmiskop I and Elmiskop II and the Hitachi HU-10 and HU-11 microscopes all have multiple projector lens pole pieces which can be conveniently interchanged during operation. These modifications all facilitate the recording of diffraction patterns and the attainment of wide ranges of magnifications. A further modification of the basic three-element lens system which is gaining wide acceptance is the use of a two-stage or "double" condenser lens of the type which was popularized by the Siemens Elmiskop I (27,28). Such a lens not only contributes to high resolution by providing accurate control over the angle of incidence of the electrons on the specimen, but also provides better control of the intensity of illumination than does the conventional single-stage lens. Of particular interest is the fact that with a double condenser lens, the diameter of the electron beam at the specimen can be reduced to as little as 2 μ. This makes it possible to attain the high intensities of illumination necessary for work at high magnifications and yet greatly reduces the total heating of the specimen due to electron bombardment. The double condenser lens can also be used to provide a fine electron source to assure sharp electron diffraction patterns, or to record two focused diffraction patterns simultaneously with a common center (28). These features are particularly useful in metallurgical work where it is frequently desirable to do diffraction studies with the electron microscope. Further improvements in

illumination may be achieved through the use of pointed filaments (29–31) and by modifying the design of the electron gun (32,33).

A majority of the first commercial electron microscopes were provided with accelerating voltages in the range of 40 to 60 kv. For the past several years, however, there has been a trend toward the use of higher voltages, and most commercial microscopes now have provisions for varying the accelerating voltage in several steps from 50 to 100 kv. While these higher voltages were introduced primarily in response to a need on the part of biologists for increased penetrating power to facilitate the examination of relatively thick microtome sections of biological materials, they have proved to be equally advantageous to metallurgists, particularly for transmission studies of thin metal foils and for identification of precipitate particles by selected area electron diffraction.

Recently there has been considerable interest in constructing instruments capable of working at even higher accelerating potentials to obtain still greater penetrating power. Several experimental instruments with operating voltages in the range from 150 to 400 kv have been described in the literature (34–37), and the Japan Electron Optics Laboratory Co. has announced a commercial electron microscope operating at 80, 100, and 150 kv (Fig. 7). Dupouy and associates (38) have recently completed a microscope capable of operating at potentials up to one million volts and have used this instrument to study living cells and to observe the internal structures of metal foils up to 3 μ in thickness. Interestingly enough, with recent refinements in microtome techniques, biologists have become interested in using accelerating voltages as low as 10 kv because of the increase in contrast that can be obtained thereby (39–41), and several manufacturers are now considering marketing instruments that will operate at these voltages.

In addition to developments in instrument design which have improved the optical characteristics of electron microscopes, there have been many improvements in the mechanical and electrical features that have greatly increased the convenience of operating and servicing the instruments. Although these vary somewhat among instruments produced by different manufacturers and are too numerous to attempt to describe in detail, a few important trends can be indicated. In general, the vacuum systems of the instruments have been greatly improved. By using high-speed pumps and efficient systems of vacuum valves, the evacuation time required after inserting photographic plates or changing specimens has been greatly reduced. Vacuum connections have been simplified and their reliability improved, reducing the incidence of vacuum leaks and making it easier to disassemble the instruments for routine cleaning and maintenance. Electrical circuits have been refined so that troubles due to causes other than the normal failure of electron tubes are rarely encountered. Modern instruments have also been designed so that accurate alignment of the electron optical elements can be achieved and maintained with little difficulty. In many, electrical beam deflecting systems adjustable from the control panel have replaced the unhandy mechanical devices for aligning the electron gun and the condenser lens. Provisions have also been made for accurately and conveniently centering apertures while the instruments are in operation, and for easily removing the apertures from the beam column for cleaning. Following the work of Leisegang (42), Rang (43), and Haine and



Courtesy of Fisher Scientific Co.

FIG. 7. The JEM-150 Electron Microscope Providing Electron Accelerating Voltages of 80, 100, and 150 kv.

Mulvey (44), most stigmators are now operated by electrical or mechanical controls located outside the microscope column. This greatly increases the ease and rapidity with which corrections for astigmatism can be effected, making it much easier to keep the instruments operating near the limit of their resolving powers.

In recognition of the long, tedious hours the electron microscopist spends at his instrument, much more consideration is being given to building microscopes for the comfort and convenience

of the operator (45). In addition, there is a trend toward the use of automatic control systems to relieve the operator of constantly having to attend to details of routine operations. Perhaps the most extensive of such developments are to be found at present in the RCA EMU-3 and the Zeiss EM-9 microscopes which have systems of automatic vacuum controls, electronic exposure meters and timers, and mechanisms which automatically change photographic plates after each exposure.

There is yet another recent trend in instrument development that is of particular interest to metallurgists. In the past, manufacturers of electron microscopes catered mainly to the interests of biologists who comprised the majority of users of electron microscopes. In so doing, primary emphasis was placed on obtaining the high resolving powers and high magnifications required for examination of fine structural details of biological materials, and little consideration was given to providing for the manipulation and treatment of specimens in the microscope, as is so often desirable in nonbiological work. With the recent increase in nonbiological applications, however, a variety of accessories have been developed for this purpose (46). These include: devices for heating, cooling, and deforming the specimens while they are under observation in the microscope; special specimen holders for tilting and rotating the specimen for stereomicroscopy and to facilitate observation of dislocations and orientation of small crystals for crystallographic studies by selected area diffraction; attachments for projection X-ray microradiography; adapters for obtaining electron diffraction patterns by the conventional transmission and reflection techniques; 35-mm cameras for survey work requiring large numbers of micrographs; and cine-cameras for recording rapid changes in the specimen during treatment. In the past, most such devices have been designed by individual microscopists to meet the needs of a particular research program. Recently, however, manufacturers of microscopes have become active in developing attachments for their instruments. As indicated in Table I, many of these attachments are already available, and many more are in the final stages of development.

Methods Using Surface Replicas:

Until recently, when the direct examination of metallurgical structures by thin film techniques became popular, most investigations of metal specimens by transmission microscopy were carried out indirectly using thin replicas prepared from surfaces of specimens that had been polished and then etched so as to reveal the microstructural features of the specimens. A number of polishing, etching, and replicating techniques developed during the past few years contributed greatly to the growth of electron metallography.

Polishing and Etching Techniques.— The techniques used in polishing metallurgical specimens for electron microscopy are usually the same as those for optical microscopy except that particular care must be taken to avoid introducing scratches, cold work, and similar disturbances into the surfaces. Because of the high resolving power of the electron microscope, defects that cannot be detected in optical micrographs appear clearly and objectionably in electron micrographs. To avoid cold working surfaces, many investigators have adopted electrolytic polishing procedures; however, these are difficult to use with many types of alloys and often cause pitting and contamination of the surfaces. Long and Gray (47) have introduced a very promising technique for

polishing metal surfaces employing the Syntron vibratory polishing apparatus (48,49) shown in Fig. 8. This apparatus consists of a stainless steel pan mounted on a magnetically driven vibrator head. The polishing cloth is firmly attached to the bottom of the pan and covered with a suspension of polishing abrasive. The specimens are weighted and placed in the pan, and the vibratory motion, which has a rotational component, causes them to move around the pan over the cloth.

Courtesy of the Syntron Co.

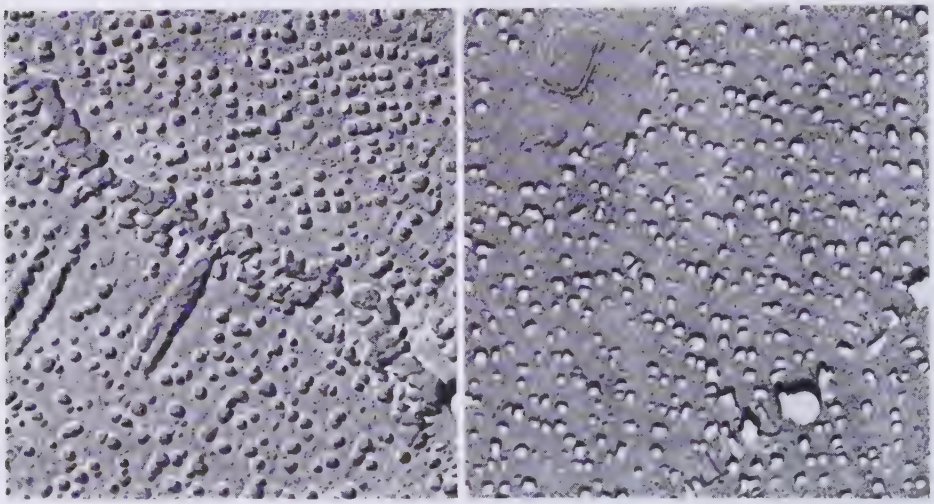
FIG. 8.—Syntron Vibratory Polishing Apparatus.

This action is very gentle; consequently it produces virtually no working of the surfaces and has very little tendency to round the edges of specimens, dislodge inclusions, or overpolish. The method is, therefore, ideally suited for preparing specimens for electron metallography and has recently been adopted by a number of laboratories for this purpose.

Etching is undoubtedly the most important step in the preparation of metallurgical specimens for examination by electron microscopy for it is the principal factor in determining the fidelity of the micrographs ultimately obtained. The simplest way to select an etchant for electron microscopy is to choose one which has previously been used successfully in optical studies of the alloy in question. Anderson has prepared an extensive compilation of etchants for a variety of metals (50). This approach does not guarantee success, however, for the etching requirements are not identical in the two cases. Because of the necessity of using surface replicas, virtually the only type of etching action which is satisfactory for electron microscopy is one that attacks the different phases of the alloy at different rates, thus bringing them into relief at different levels in the surface. Selectively staining, roughening, or dissolving certain phases or severely attacking interfaces between different microstructural features usually produces satisfactory optical contrast but generally does not provide surfaces suitable for replication. Furthermore, since structural details that cannot be detected optically can be studied by electron microscopy, etching for electron microscopy must be effective on a correspondingly finer scale. In recognition of these difficulties, Subcommittee XI of ASTM Committee E-4 has carried out a program on electron metallographic techniques which has involved in part the evaluation of etchants for steels (3), titanium alloys (7), and certain high-temperature alloys (8). Articles describing etching techniques for electron metallographic studies of aluminum alloys (51), steels (52–54), iron-nickel alloys (55), heat-resistant alloys (56,57), and magnesium alloys (58) have also been published. Etchants for other types of alloys can be found in articles describing studies of the alloys. Two rather different types of etching procedures have recently been proposed for electron metallography. The first of these is a selective etching procedure; the second is gas ion bombardment etching.

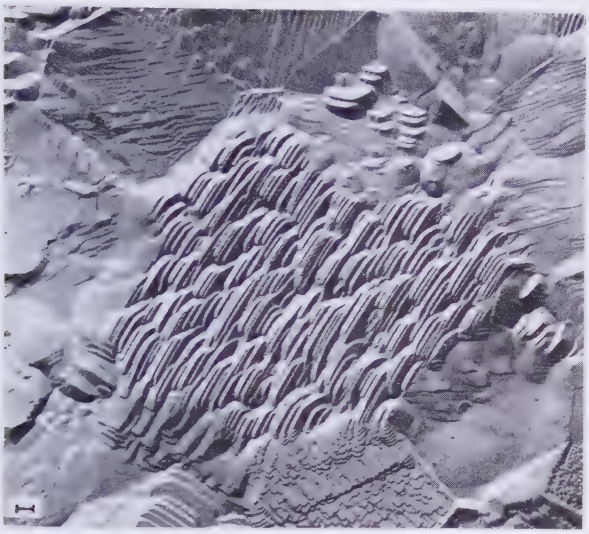
While numerous selective etching and staining procedures have been developed for optical metallography, only one has been reported to date for electron metallography. This one preferentially attacks particles of the age-hardening, intermetallic phase of nickel-base heat-resistant alloys, permitting them to be distinguished from particles of various carbides and nitrides which also form in these alloys (59). Figure 9 illustrates this procedure. The micrograph in Fig. 9(*a*) was taken from a specimen of a nickel-base alloy which was etched in the normal manner so that all precipitate particles stand in relief above the matrix phase. Figure 9(*b*) shows the same specimen after application of the selective etching procedure dissolved the γ' particles, leaving depressions in the surface at the positions they originally occupied. Comparison of these two micrographs clearly shows the relative distribution of the γ' and carbide and nitride particles in this specimen. Although this selective etching procedure is of rather limited applicability, others of wider applicability will undoubtedly be discovered in the future and will greatly increase the usefulness and versatility of electron metallographic investigations.

Etching by gas ion bombardment, or "vacuum cathodic etching," consists of removing metal from the surface of the specimen by bombarding it with ions of an inert gas such as argon or krypton in a cold cathode gas discharge. Usually the gas discharge is generated by imposing a potential of about 4000 v between the specimen and an aluminum or zirconium anode plate in a chamber containing the etching gas at 5 to 50 μ pressure. Early vacuum cathodic etching units (60–63) were incorporated in the bell jars of high-vacuum evaporators. Recently, however, units of simplified design have been described (64,65) which are less expensive to build and which provide for easier control of the variables



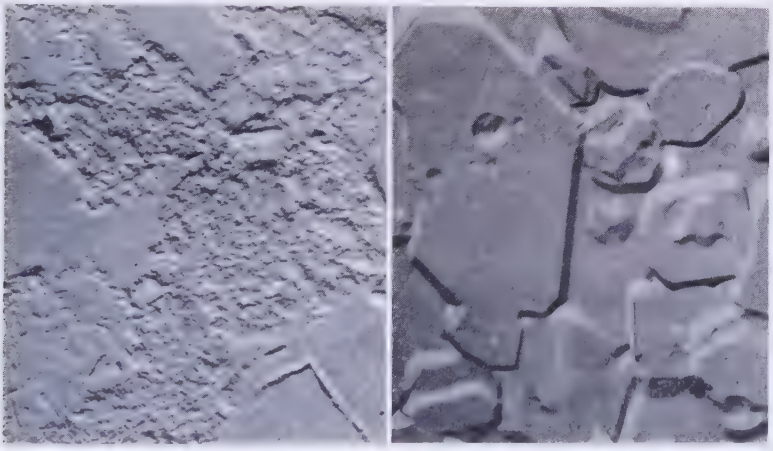
(*a*) Preliminary etch; all minor phases in relief. (*b*) Selective etch; carbides in relief, γ' particles etched out.

FIG. 9.—Selective Etching Procedure for γ' Phase of Nickel-Base Heat-Resistant Alloys (× 16,000).



Courtesy of T. K. Bierlein, Hanford Laboratories Operation, The General Electric Co

FIG. 10.—Vacuum Cathodically Etched Specimen of Zircaloy-2 (× 2500).



Courtesy of T. K. Bierlein, Hanford Laboratories Operation, The General Electric Co.

(*a*) Porcelain (× 8000). (*b*) Cermet (× 6000).

FIG. 11.—Vacuum Cathodically Etched Specimens.

influencing etching. The apparatus of Newkirk and Martin (64) employs a magnetic coil which causes the electrons in the gas discharge to follow curved paths, thus increasing the probability of ionization and the efficiency of etching, and Bierlein (66) has recently reported that a high-frequency electrostatic field can also be used effectively for this purpose. Calbick (67) has described a more

elaborate apparatus that uses a very strong magnetic field, and develops high ion currents with low voltages and high gas pressures.

Several advantages have been cited for vacuum cathodic etching, the more important ones being: the same apparatus and nearly the same etching conditions can be used for a variety of different materials; nonhomogeneous materials such as metal couples, cermets, and porous sintered compacts can be etched readily; and surfaces are free of contamination when properly etched. Tsuchikura and associates (63) and Bierlein (65) both applied the technique to stainless steels and similar alloys, and applications to aluminum, steel, and other metals have been reported by other investigators (68–70). An electron micrograph of an annealed specimen of Zircaloy-2 prepared by vacuum cathodic etching is shown in Fig. 10. Bierlein (65) also showed that the method could be used with nonconducting materials and applied it in studies of ceramics and ceramic-metal products. The electron micrographs in Fig. 11 show the excellent microstructural detail developed in these types of materials by this etching technique. Fert (71) suggested the use of ion bombardment as a method of reducing surface contamination in electron diffraction and in reflection microscopy. Subsequent observations by Trillat (72) and Ladage (73) showing that ion bombardment could cause certain physical and chemical changes in the surfaces have led to a number of studies of the effects of gas ion bombardment on various materials (74–83), and on its use in preparation of specimens for electron diffraction and electron microscopy (84–87).

Replica Techniques.—While it might be thought that the use of replicas would introduce experimental difficulties and cause loss of resolution, this generally is not the case, for a number of replica techniques have been developed which are remarkably convenient to use and which give adequate resolution for most metallurgical applications. Instead, the major problem is usually that of finding etchants which will reveal microstructural details faithfully and on a scale as fine as can be reproduced by the replicas. While a variety of different types of replicas have been developed, shadowed plastic replicas of Formvar or collodion appear to have been used in a vast majority of metallurgical studies. The popularity of these plastic replicas results from the fact that they are simple to prepare, have good contrast, and yield micrographs which are pleasing in appearance and which can be easily interpreted in terms of the contours of the surface of the specimen. Studies by Agar and Revell (88) have largely justified this popularity, for they have shown that properly prepared Formvar replicas have excellent elasticity and strength and are capable of better than 100 Å resolution. It should be emphasized that replicas of the order of 500 to 700 Å in thickness must be used to attain this resolution. It is probable that in most ordinary investigations replicas of the order of 1000 Å thickness are used and resolution is reduced to about 200 Å due to electron scattering within the body of the replicas. While this order of resolution is still adequate for most metallurgical investigations, Agar and Revell (89,90) have described techniques for reproducibly preparing the thinner replicas and for stripping them from surfaces without distortion or tearing.

During the past few years there have been two new developments of major importance in replica techniques: the introduction of the carbon replica film, and the development of the extraction replica technique.

Carbon films were first described for support membranes and replicas for

electron microscopy around 1950 (91,92); however they received little attention and were virtually unused until 1954 when Bradley (93) developed a simple and convenient method for preparing them and clearly demonstrated their advantages over other materials. Bradley's method utilizes an apparatus of the type shown in Fig. 12 which is mounted in an ordinary vacuum evaporator. After the system is evacuated, a current of about 50 amp is passed through the carbon rods. This produces intense heating at the tip of the pointed rod, causing carbon to evaporate and deposit in a thin film over the specimen. The thickness of the film is judged by observing the color developed on a white porcelain plate. Films about 50 Å in thickness are just detectable, while films 200 to 300 Å have a dark brown color. A drop of high vacuum pump oil placed on the plate facilitates observation of the color of the film since the carbon does not form a film over the oil. Carbon films formed in this way possess many characteristics which make them ideally suited for electron microscopy. They are exceptionally strong, virtually structureless, extremely stable in the electron beam, and unaffected by most reagents and solvents used in preparing and treating

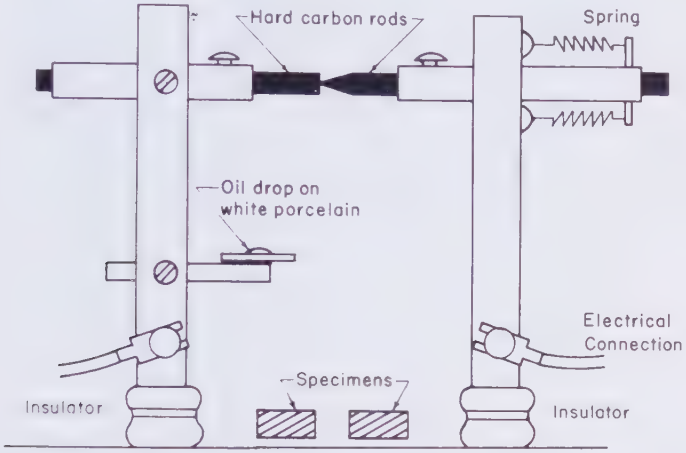
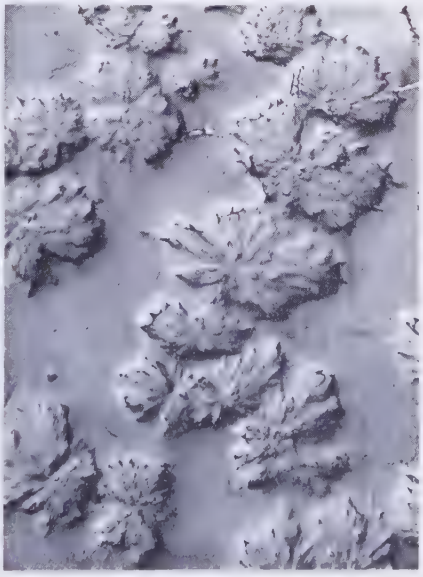


FIG. 12.—Diagram of Bradley's Apparatus for Evaporation of Carbon Films.



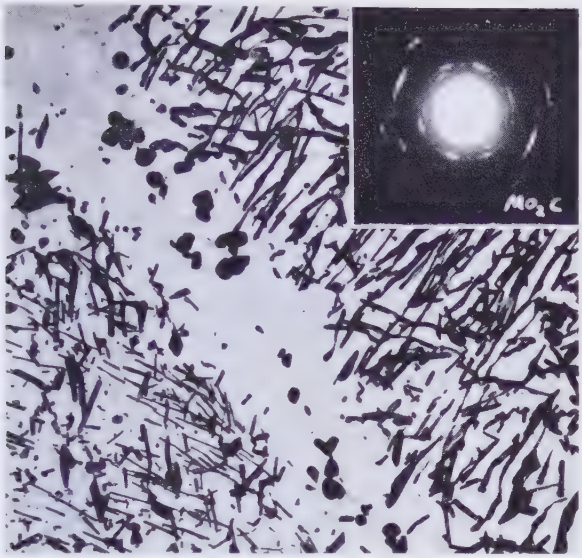
Courtesy of Y. E. Smith, Department of Chemical and Metallurgical Engineering, The University of Michigan.

FIG. 13.—Electron Micrograph Showing Whisker Growth on Sintered MnS Particles. Palladium-shadowed carbon replica (× 5000).

specimens. In addition, they can easily be seen against a white background and are therefore readily manipulated, even when only 30 to 50 Å in thickness.

Carbon replicas of metallurgical specimens are usually prepared by one of three different basic procedures. In a limited number of cases it is possible to strip the films directly from the specimen (94,95). Alternately, the specimen may be dissolved away from the replica film by means of a suitable reagent (93–96). This latter procedure has also been used in studies of a variety of different biological materials, minerals, pigments, and fibers (97). Figure 13 shows an electron micrograph of a sintered MnS particle that was obtained from a carbon replica prepared in this way. Thin (30 to 50 Å) replicas prepared by these two methods may provide resolutions of better than 20 Å; however, considerable skill and experience is required to achieve this level of performance. The most common method of preparing carbon replicas for electron metallography is carried out in two stages. First, a primary plastic replica of the surface is prepared and mounted on a specimen grid in the usual manner. The plastic replica is then coated with carbon and finally the plastic is dissolved away, leaving only the secondary carbon replica film on the grid. Details of procedures for carrying out this process with variations for obtaining positive and negative shadowing have been described (97–100). It is interesting that resolutions in the range of from 20 to 50 Å have been obtained with very thin carbon replicas prepared in this way (97–99) using Formvar primary replicas. This indicates clearly that Formvar replicas reproduce surface topology with high accuracy and suggests that the poorer resolution which they exhibit when observed directly in the microscope results from excessive diffuse scattering of electrons due to their greater thickness (88,97). Using the Formvar-carbon replica process, Smith and Nutting (99) have observed precipitate particles and subgrains in alloy steels with diameters of about 100 and 500 Å respectively. Carbon replicas have thus contributed greatly to the improvement of resolution in electron metallography, and are rapidly surpassing all other types of replicas in popularity. Because of their unusual properties and their increasing popularity, several studies have been made of the mechanism of evaporation of the carbon films and of their structures and physical properties (101–107), and there have been a number of papers describing modifications of the technique for preparing carbon replicas (98,108–119).

The extraction replica technique (120) provides a very effective method for isolating precipitate particles from multiphase alloys for study by electron microscopy. In preparing an extraction replica, the specimen is given an initial etching treatment such that the precipitate particles protrude in relief from its surface; a replica film is then applied and the specimen is etched a second time with the replica in place. The second etching treatment serves to free the replica and the precipitate particles from the surface. Since the particles were partially embedded in the replica, they remain attached to it and can be observed directly in the electron microscope, while the general microstructure of the specimen is revealed by the replica in the usual manner. This provides an excellent way of observing the actual size and shape of the precipitate particles and for determining their distribution in the plane of the specimen. A particular advantage of the technique arises from the fact that electron diffraction patterns can be obtained from the particles by selected area electron diffraction, as



Courtesy of R. M. Fisher, Edgar C. Bain Laboratory for Fundamental Research, U. S. Steel Corp.

FIG. 14.—Electron Micrograph and Selected Area Electron Diffraction Pattern of Mo_2C Particles Isolated from a 3.2 per cent Molybdenum Steel by the Extraction Replica Technique (× 16,000).

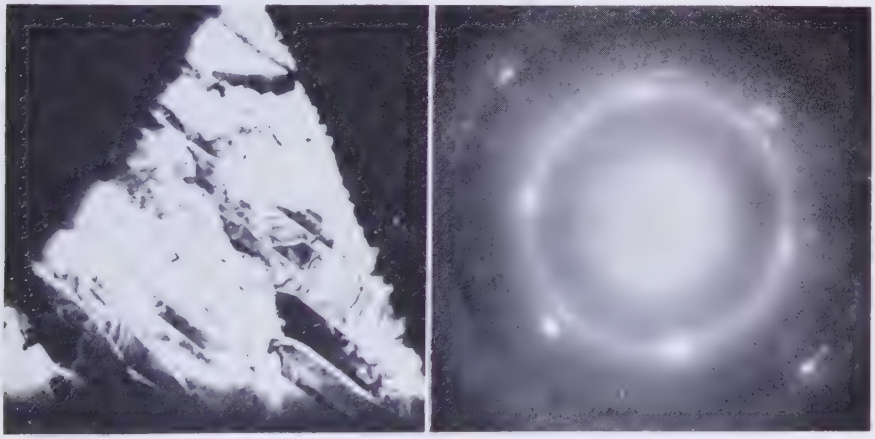


FIG. 15.—Electron Micrograph (× 8000) and Selected Area Electron Diffraction Pattern of Plate-Like $M_{23}C_6$ Carbide Particles Isolated by the Extraction Replica Technique from the Intergranular Fracture Surface of a Nickel-Base Heat-Resistant Alloy Specimen.

illustrated in Fig. 14. This is undoubtedly the most conclusive method presently available for identifying precipitate particles of alloy systems. In practice, the method is limited to relatively small particles, for larger ones are usually embedded so deeply in the specimen that they are not freed by the etching treatment; however, extensive networks and relatively large particles of

grain boundary precipitates can often be isolated from fractured surfaces where the fracture was caused to occur through the grain boundaries (121) as illustrated in Fig. 15. Difficulty is also encountered in obtaining electron diffraction patterns from the larger particles and it is here that the greater penetrating power provided by accelerating voltages of 80 to 100 kv is a decided advantage. Carbon films are particularly well suited for preparing extraction replicas, and methods for using them in this way have been described in detail (122–126). Devices for tilting and rotating specimens during observation have also been described in the literature (127,128) and are commercially available for some electron microscopes. These devices allow principal crystallographic axes of crystalline particles to be placed in preferred orientations relative to the electron beam so that diffraction patterns of high symmetry can be obtained to facilitate identification and structural studies of the particles.

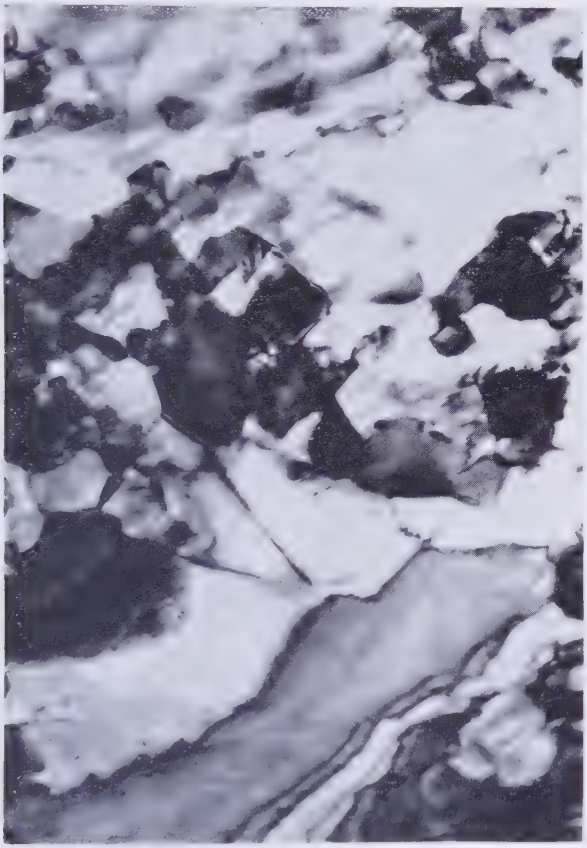
To date, extraction replica techniques have been used most extensively in studying precipitation and aging processes in various types of steels (123–142) although applications to other types of alloys have also been reported (143–145). The use of this technique has already contributed significantly to understanding precipitation processes and phase transformations in steels, and it can be expected to find increased application to other alloy systems in the future.

In addition to the carbon and extraction replica techniques, a number of other interesting and useful replica techniques applicable to metallurgical studies have been developed during the past several years. Procedures have been described for replicating a preselected area of a surface and for preparing successive replicas from the same area (146–150) as well as for replicating rough, porous, curved, angular, or interior surfaces (151–156), fine particles, crystals, and whiskers (157–159), water-sensitive materials (160), and radioactive surfaces (161). An improvement on the method of Grube and Rouze (162) using a parting layer of a surface active agent in separating replicas from surfaces has been described by Long and Bridges (163), while Boswell (164) describes the use of B_2O_3 for similar purposes. These techniques are particularly useful in the direct stripping of carbon and silica replicas from metal surfaces, although they may cause some loss in resolution. Other uses of surface active agents in replica processes have been described by Haanstra (165). Hibi and Yada (166) have described an interesting technique for the preparation of replicas at liquid nitrogen temperature. Various techniques involving carbon replicas have been summarized by Cosslett (101), Bradley (97,98), Comer (109), and Fukami (110) while a number of other replica techniques of general interest and applicability in electron metallography have been described recently by others (98,167–183).

The increased resolution provided by carbon replicas has stimulated considerable interest in high-resolution shadowing. Platinum was generally accepted as the best material for this purpose for a number of years; however, Bradley (113) has reported that the simultaneous evaporation of platinum with carbon provides better resolution with less background structure and less granulation at high beam intensities. Procedures for platinum-carbon shadowing have been described in detail by Bradley (98,113) and others (111,112,116). Murphy and Goodman (184) have recently reported that osmium oxide also is less crystalline than platinum and gives better resolution in some cases.

Transmission Studies of Thin Metal Films:

The first studies of thin metal films by transmission electron microscopy were reported in 1949 by Heidenreich (185) who observed subgrain structures of the type shown in Fig. 16 in thin films of aluminum and an aluminum-copper alloy, and who subsequently studied the relations of these structures to cold work and recovery processes (186). Because of the difficulties involved in preparing metal films thin enough to transmit electrons, only a few further investigations of this kind were reported until 1956 when Hirsch, Horne, and Whelan (187,188) and Bollman (189,190) demonstrated that dislocations, their movements, and their interactions could be observed by high-resolution studies of thin metal films. These results immediately stimulated an interest in thin film techniques that has grown steadily in the intervening years until today these techniques are among the most widely used in electron metallography.



Courtesy of H. Fernandez-Moran, Mixter Laboratories for Electron Microscopy, The Massachusetts General Hospital.

FIG. 16. Transmission Electron Micrograph of a Thin Slice of Tin Prepared with an Ultramicrotome Using a Diamond Knife (× 85,000)

One of the biggest problems in thin film studies is the preparation of the films

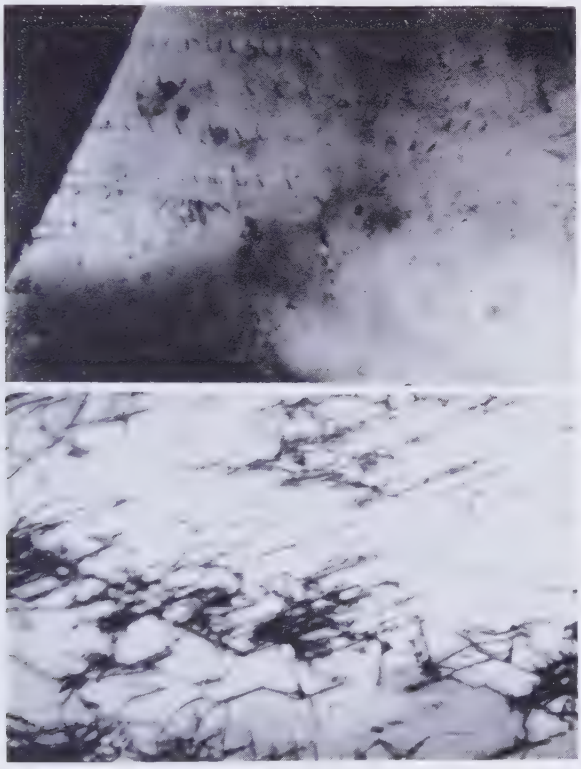
themselves, and several different methods have been developed for this purpose. In the most widely used of these, a piece of metal foil initially a few thousandths of an inch thick is carefully electropolished until areas sufficiently thin to transmit electrons are obtained. A number of special procedures and devices have been developed for carrying out this electropolishing operation (190–195). Other commonly used methods include electrodeposition (196), chemical thinning (187,197) and vacuum evaporation (198–200). All of these methods have been used for a number of years to prepare metal films for transmission electron diffraction investigations (201); however, three somewhat more unusual methods have been developed for electron microscopy. Castaing (202) has described the preparation of thin films of a number of metals by bombarding foils with gas ions. Since the action of the ion bombardment is relatively slow, it is generally used only as the final thinning operation following preliminary thinning by electrolysis. The advantages of this method include most of those cited above for vacuum cathodic etching. Takahashi, Ashinuma, and Watanabe (203) have prepared films of a variety of pure metals and alloys by slowly withdrawing a small wire loop from the molten metal or alloy using a furnace which can be evacuated or filled with an inert gas to prevent oxidation of the films. Moran (204) developed an ultramicrotome with a diamond knife which is capable of sectioning a number of metals and alloys. Subsequent studies (205–208) have shown that although the sectioning may introduce some mechanical disturbance, the films obtained are suitable for many purposes. Figure 16 is a transmission micrograph from an ultramicrotome section of tin. This method has also been applied to sintered metal powders and to hard, brittle substances such as aluminum oxide and silicate powders (209,210). Kelly and Nutting (211) developed an electrolytic machining technique for producing foils from thicker specimens, and Strutt (212) has described several modifications for cutting slices from large metallographic specimens and for thinning them without introducing mechanical deformation, allowing thin film studies to be made of the structures of bulk specimens that have been heat treated, deformed, and examined by ordinary metallographic procedures. Detailed discussions of these techniques are also given in recent books on electron microscopy (213,214).

Thin film studies have been largely responsible for the development of devices for deforming, heating, cooling, and tilting specimens in the electron microscope. In their initial studies of thin metal films using a Siemens electron microscope, Hirsch and associates (187,188) observed that dislocations could be caused to move, presumably under the influence of thermal stresses, when the electron beam was concentrated onto a small area of the foil with the double condenser lens, and that the intensity of illumination was sufficient to permit the image on the fluorescent screen to be photographed with an external movie camera using high-speed film. Shortly thereafter, Wilsdorf (215) developed a specimen holder for the Philips EM-100 electron microscope which allowed tensile or compressive stresses to be applied to the specimen mechanically, and employed this device to show the movement and interaction of dislocations in high-purity aluminum from the annealed state to fracture and to demonstrate the existence and operation of various types of dislocation sources in thin films of 18-8 stainless steel (216). The interesting results obtained in these studies stimulated

the development of devices for treating specimens in other models of electron microscopes (217–227). As indicated previously, a variety of such devices are now available as accessories for the various commercial instruments (see Table I).

Applications of Transmission Electron Microscopy:

A comprehensive survey of recent metallographic investigations involving transmission electron microscopy is beyond the scope of this article. The following discussion is intended only to indicate the general areas of metallurgical research in which electron microscopic techniques are being used most extensively at present, and to describe briefly the type of information which electron microscopy has contributed in each case.



Courtesy of P. B. Hirsch, Cavendish Laboratory, The University of Cambridge.

FIG. 17 Transmission Electron Micrographs of Thin Foils of Slightly Deformed Stainless Steel (× 22,500).

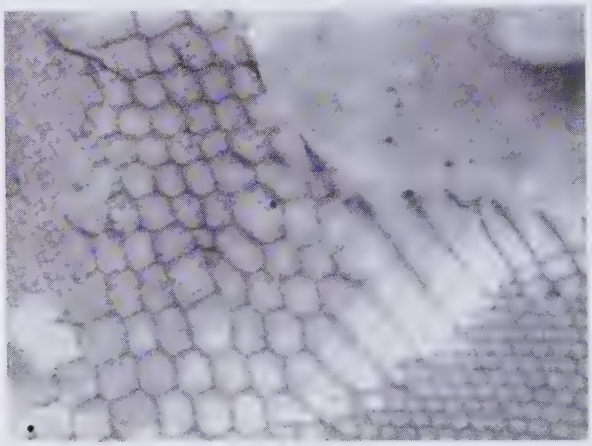
(*a*) Foil deformed about 0.8 per cent in tension, showing pile-ups of dislocations at a grain boundary.

(*b*) Specimen deformed 2 per cent by rolling, showing irregular array of dislocations.

and these are being used almost routinely in numerous investigations of the mechanisms whereby impurities, inclusions, structural defects, and precipitate particles interact with dislocations to influence the mechanical properties of metals and alloys.

More detailed summaries of experimental results may be found in the various review articles cited; in addition, a remarkably complete and up-to-date collection of abstracts of articles on electron metallography is published monthly in the subsection on "Structures déterminées au moyen des électrons," of Section 6 on "Structure des solides et des fluides," of the *Bulletin Signalétique* (previously the *Bulletin Analytique*), which is prepared by the Centre de Documentation du Centre National de la Recherche Scientifique, Paris, France.

As indicated above, many of the most interesting and theoretically significant results in transmission electron metallography during the past few years have been obtained in studies of thin metal films. By providing a direct experimental method for observing dislocations and similar structural defects, thin film techniques have afforded a means for investigating, testing, and refining many of the concepts relating to the movement and interactions of dislocations that had previously been based largely on indirect evidence and theoretical considerations. For example, the various early investigations of aluminum and stainless steel (186 – 190,216,228 – 234) showed characteristic differences in these metals, and provided confirmation of several of the fundamental concepts of dislocation theory. In the annealed condition both metals were found to be relatively free of dislocations. Small amounts of deformation produced dislocation pile-ups at the grain boundaries in stainless steel. With larger amounts of deformation the pile-ups were replaced by dislocation networks, as shown in Fig. 17, and subsequently by stacking faults and twin boundaries. In general, dislocation movement in stainless steel was found to be confined to slip planes, and no cross slip or climb was observed except at grain boundaries, although the splitting of dislocations into partial dislocations with the formation of stacking faults was frequently observed. In aluminum, on the other hand, cross slip and climb occurred readily so that dislocation movement was not confined to slip planes, and well-defined, low-energy sub-boundaries were formed. In a num-

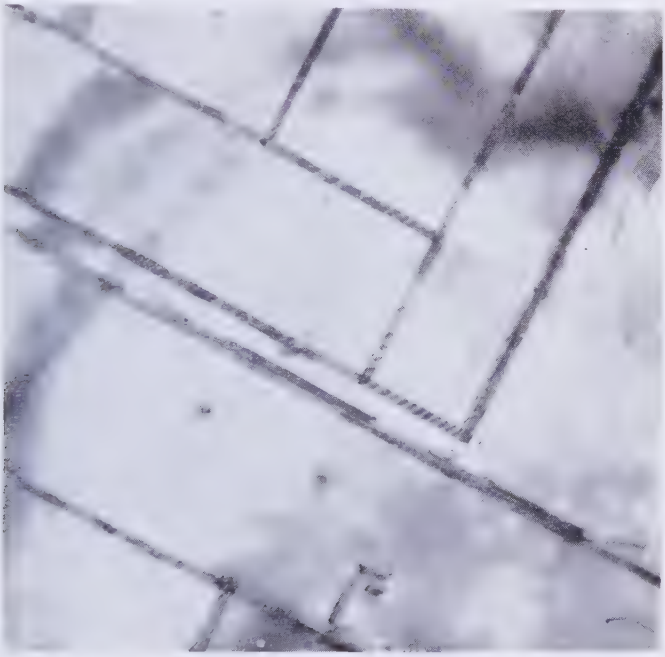


Courtesy of A. S. Keh, Edgar C. Bain Laboratory for Fundamental Research, U. S. Steel Corp.

FIG. 18.—Regular Network of Dislocations in a Deformed and Annealed Single Crystal of an Fe-3Si Alloy (× 57,000).

ber of cases, simple tilt and twist boundaries were observed and these were found to consist of lines and hexagonal networks of dislocations, similar to the one shown in Fig. 18, as predicted by theory. In addition, the spacing of dislocations in these boundaries was found to be in satisfactory agreement with predictions based on the relative misorientations of the grains involved as determined by selected area diffraction. These differences in the movement and arrangement of dislocations were in agreement with theoretical predictions based on the fact that the stacking fault energy is relatively high for aluminum but relatively low for stainless steel (about 200 ergs per sq cm and 13 ergs per sq cm, respectively). More recently (235,236) it has been found that face-centered cubic metals such as gold, copper, and nickel which have intermediate stacking fault energies (from 30 to 90 ergs per sq cm) show intermediate behavior in that cross slip and climb occur readily but subgrain structures which form are relatively poorly developed compared to those found in aluminum.

Using his device for deforming thin films while they are under observation in the electron microscope, Wilsdorf (216) made extensive studies of the generation of dislocations in stainless steel and obtained micrographs showing dislocations originating from nearly all types of dislocation sources predicted by theory, including grain boundaries, twin boundaries, polygonization boundaries, precipitate particles, and classical Frank-Read sources. His studies of the deformation of thin films of aluminum from the annealed condition to fracture re-



Courtesy of R. Marcus, Department of Chemistry, The University of Michigan.

FIG. 19. Stacking Faults in Thin Single Crystal Film of Copper Formed by Evaporating Copper on a Rocksalt Crystal (× 29,000).

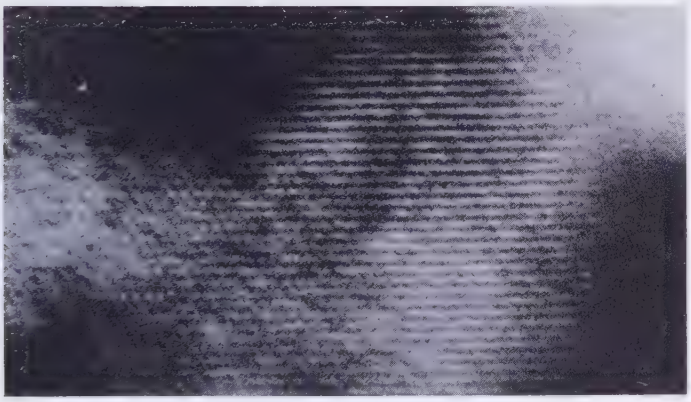
vealed slip mechanisms for small amounts of deformation which were in agreement with those described above; in addition, very complex arrays and interactions developed in the highly deformed foils just prior to fracture, and three different fracture mechanisms were observed. Pashley (217) reported similar studies of the fracture of gold films, and reached the interesting conclusion that the tensile strengths of the thin films were several times the normal bulk tensile strength of gold.

Thin film techniques have also been found to be uniquely suited for observation of a number of other types of structural defects, including antiphase domains and boundaries (237–239), superdislocations (240), the periodicity and related features of ordered alloy structures (241 – 243), thermal vacancies (244,245), growth spirals and defects (246–248), dislocation loops (233,234,249,250), stacking faults (231,251), paired screw dislocations (252), and twins (253–255). Figure 19 shows an interesting case where extended stacking faults were observed in thin single crystal films of copper prepared by evaporating the copper on an etched surface of a rock salt single crystal (256). Stacking faults would normally not be expected in pure copper because of the relatively high stacking fault energy; however, their occurrence in these films may be related in some manner to the epitaxial relation of the copper to the rock salt substrate during formation and subsequent manipulation of the films.

The fact that individual dislocations and similar structural features can be observed directly in the electron microscope has directed considerable interest to the phenomena responsible for the contrast that renders these features so clearly visible. In their first papers on the subject, Bollman, Hirsch, Horne, and Whelan (187-190) suggested that the visibility of individual dislocations in thin metal foils could be attributed to the strained condition of the crystal lattice in the regions immediately surrounding the dislocations. This strain or distortion of the lattice has the effect of relaxing slightly the conditions for diffraction of electrons and, for certain orientations of the foil relative to the electron beam, permits a larger number of Bragg reflections to occur from the strained regions than from the adjacent unstrained portions of the crystal. The diffracted rays are generally sufficiently divergent to be intercepted by the objective aperture, and since they may involve a considerable fraction of the incident intensity, the dislocations may contrast rather sharply with the surrounding crystal, appearing usually as fine dark lines in the electron micrographs (see Fig. 17). Recently several papers have been published in which the theory of the diffraction effects which occur at dislocations and other imperfections in thin crystalline films are described more rigorously and in greater detail (257–261), with the application of dynamical scattering theory to account for contrast features that cannot be treated by the kinematic theory.

Dislocations and similar imperfections can also be revealed in thin metal films by another means. As indicated previously, Menter (262) showed that individual lattice planes, dislocations, and other lattice imperfections could be resolved by transmission studies of thin crystals of substances having rather large interplanar spacings and favorable distributions of heavy atoms in the crystal structure. The smallest interplanar spacing which has been resolved in this way to date is 5.63 Å (15), which is considerably greater than the spacings of interest in most metal crystals. It has also been demonstrated (199) that lattices having spacings less than this can be resolved indirectly by means of moiré patterns

which are formed by interference beat effects when two crystals with the same lattice spacing are intimately superimposed with slight misorientations or when crystals with slightly different spacings are superimposed with the same orientation (see Fig. 20). Dislocations appear distinctly in such moiré patterns (199,264), and Bassett, Menter, and Pashley (199) showed that such moiré patterns reveal dislocations clearly, and can therefore be used to study dislocation densities and to follow the movement of dislocations in metal foils. Although the preparation and handling of the metal films to obtain moiré patterns involves some special difficulties, this method has the advantage over those described above in that the components of the Burgers vectors of the dislocations can be deduced more easily. Menter (265) has reviewed the characteristics and potentialities of studies involving moiré patterns, and the theoretical basis for the interpretation of these patterns has been described in several other papers (266–270).



Courtesy of H. Fernandez-Moran, Mixter Laboratories for Electron Microscopy, The Massachusetts General Hospital

FIG. 20. Moiré Pattern from Superimposed Monocrystalline Gold Films (× 180,000).

Thin film techniques are particularly advantageous for studying phase transformations and precipitation processes in metal systems, for it is possible to combine selected area electron diffraction studies with the electron microscopic observations to determine the identity, form, distribution, and relative crystallographic orientations of the phases involved, and to observe the influence of such factors as stress and temperature on these variables. Some of the first work of this kind was carried out by Castaing (202) and Takahashi and associates (203,271-273) who reported studies of a number of different alloys ranging from the frequently studied 4 Cu aluminum alloy to complex nickel-base heat-resistant alloys. Subsequently, similar investigations of several alloys of aluminum (274–278), copper (279), titanium (280), and of steel (281–284) were reported by others, and the same general techniques were employed to study the carburization of aluminum and the diffusion of carbon in iron and aluminum (285), the "de-zincification" of brass (286), and the segregation of sulfur at the grain boundaries in iron (287). A particular advantage of this method is that diffraction effects enhance contrast so that it is possible to detect particles of new phases which would be much too

small to be revealed by most etching techniques. Figure 21 shows extremely small particles of $Fe_{16}N_2$ in iron containing 0.02 per cent nitrogen. Nicholson and Nutting (288) have shown that it is even possible to observe the strain fields which develop around Gunier-Preston [2] zones and to detect G.P. [1] zones which are only one atom layer thick and of the order of 50 Å in diameter. Subsequent investigations (275,289) have shown that the interactions of dislocations with

Courtesy of A. S. Keh, Edgar C. Bain Laboratory for Fundamental Research, U. S. Steel Corp.

FIG. 21.—Particles of $Fe_{16}N_2$ Precipitated on the {100} Planes of an Fe-0.02N Alloy (× 30,000).

precipitate particles can be observed, and the results reported to date indicate that dislocations are able to move through G.P. zones and coherent or partially coherent particles, but that they loop around noncoherent particles as predicted by theory. Cahn and Nutting (290) have also discussed the possibility of determining the amount of a precipitated phase present from measurements on micrographs obtained from thin films, and Takahashi et al (291) have described an apparatus for recording selected area diffraction patterns and electron micrographs on alternate frames of 16mm movie film to facilitate studies of phase transformations in thin films.

Thin film techniques thus make it possible to observe fundamental structural details which cannot be observed by any other currently available methods. In addition, they have great potential applicability to many practical metallurgical problems and are presently being used on a semi-routine basis in many laboratories to supplement or replace the more conventional replica studies. It is not surprising, therefore, that a considerable number of articles describing electron microscopic studies of thin metal films have been published during the past few years, and it is to be expected that work on thin films will continue at a high level for a number of years to come. The above discussion describes only in a general way some of the more interesting types of investigations for which thin film techniques are particularly well suited. More detailed descriptions of recent work by these techniques may be found in various books and review articles devoted to this subject

(139,191,213,292–298) and in collections of papers on thin films which have been published in the August 1959 issue of the *Journal of the Institute of Metals*; in "The Structure and Properties of Thin Films," John Wiley and Sons, Inc., New York, N. Y. (1959); in Vol. I of the "Proceedings of the Fourth International Conference on Electron Microscopy" (Berlin, 1958); in the "Proceedings of the European Regional Conference on Electron Microscopy" (Delft, 1960); and in the "Proceedings of the Fifth International Congress for Electron Microscopy" (Philadelphia, 1962).

Although the applications of thin film techniques are enjoying much publicity and popularity at present because of their unique and fundamental contributions to understanding of deformation, transformation, and precipitation processes in metals, many interesting and important results have been obtained in general studies of the microstructures of various metals and alloys by replica techniques. In this regard, steels have undoubtedly been investigated more frequently, more thoroughly, and more successfully than any other type of alloy. In one of the first electron microscopic investigations of steel, Mehl (299) successfully resolved the structure which, on the basis of previous optical studies, had been designated as primary troostite, and showed that it was in fact a fine pearlitic structure. Subsequently, electron microscopy has been used to reveal the submicroscopic details of the bainitic structures and to follow the microstructural changes which occur during tempering of bainitic and martensitic steels. Through the use of selected area diffraction and extraction replica techniques in this latter work it was possible to show that a fine precipitate of hexagonal epsilon iron carbide precedes the appearance of cementite in the decomposition of martensite during tempering. More recently, electron microscopic studies have shown that the carbide particles in pearlitic structures are not exclusively plate-like in form, as has been commonly assumed, but are more often lath-like rods. Nutting (300), Schrader (131,301), Habraken (135), and Grube (5) have presented excellent reviews of these and other general developments in the electron metallography of steels.

With the microstructural characteristics of the plain carbon steels fairly well understood, recent investigations have been concerned more with studying the microstructures and identifying the precipitates which form during tempering various alloy steels, with determining the mechanisms of the various precipitation and transformation reactions which occur in the heat treatment of steels, and with relating the mechanical properties of steels to their microstructures. Nutting (99,130,300,302) and Schrader (131, 301,303) have reviewed a number of investigations of alloy steels while others have been reported by Hale (140), Fourdeux (133), Habraken (135,304), Williams (305), Hagel (306), and Buhr (307) and their associates. In general, it appears that alloy steels containing non-carbide-forming elements undergo microstructural changes similar to the plain carbon steels, although the alloying elements may alter the size of the ferrite grains and carbide particles formed on tempering (130). Steels containing such elements as chromium, molybdenum, vanadium, and tungsten may develop carbides of these elements which change their microstructures and influence their mechanical properties. For example, Nutting (130) observed that the secondary hardening of a 0.2C,1.0Cr,0.5V, 0.5Mo steel upon tempering depended on the occurrence of a dispersion of very fine particles of carbides throughout the ferrite grains; MacLean (308) found that

a fine dispersion of TiC particles controlled the creep strength of a Cr-Mo-Ti steel; and Hale (**140**) found a general correlation between the dispersion of precipitate particles and the creep properties of a superheater tube steel. The studies by Ross, Sernka, and Jominy (**309**) of the relationships between microstructure and torsional strength, the investigation of the role of carbon in temper embrittlement by Mikus and Siebert (**310**), and the study of the mor-

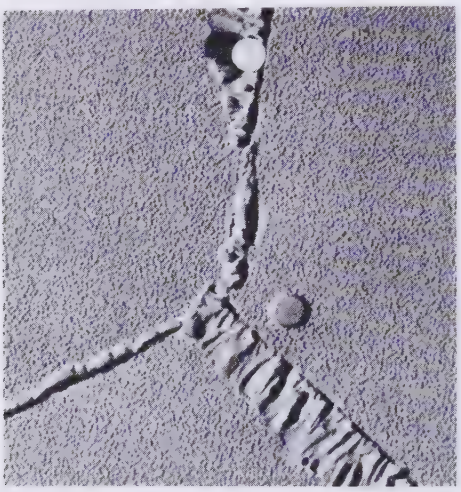


FIG. 22.—Microstructure of an Age-Hardened Nickel-Base Heat-Resistant Alloy (× 16,000).

phology of brittle fracture in steels by Turkalo (**311**) are examples of recent work to relate mechanical properties and microstructures. Fisher and associates (**136,312**) have recently made a careful reexamination of the structure and morphology of carbide precipitates in iron and low-alloy steels, while a number of other recent investigations have been concerned with the structure and mechanism of bainite formation and the martensite transformation (**138, 282-284,313-315**). One interesting result of these investigations has been the observation, by both thin film techniques and conventional replica studies, of striated or banded regions in martensite needles. The striations or bands are of the order of 100 Å in width, and are thought to arise from a highly twinned structure. These results have interesting implications regarding the formation and properties of martensite. In addition to these types of applications which are more or less theoretical in nature, electron microscopy is finding increasing use in developmental and service areas of the steel industry. These applications have recently been discussed in an interesting article by Pellissier (**316**).

The stainless steels and heat-resistant alloys are also being studied rather extensively by electron microscopy (**8,56–59,143–145,317–335**) and again the results are showing previously unobserved structures, new phases are being identified, and relations between properties and microstructures are being discovered. For example, combined electron diffraction and electron microscopic studies of a 16Cr,25Ni,6Mo steel revealed an interesting transformation of the precipitated carbides from $M_{23}C_6$ to M_6C during aging at temperatures from 1200 to 1600 F, but also showed that the hardness of the alloy was not dependent on the predominant type of carbide present but only on the distribution of the carbide particles in the matrix grains (**322**). Electron metallographic techniques have been used to particular advantage in studies of the age-hardening nickel-base heat-resistant alloys. Reflection and selected area electron diffraction techniques have been used to identify the phases which precipitate at the grain boundaries and within the matrix grains of these alloys during various heat treatments, and the form and distribution of the precipitate particles have been studied by electron microscopy. A typical microstructure for these alloys is shown in Fig. 22. The fine precipitate particles

which occur within the matrix grains are particles of an intermetallic phase designated as γ' whose crystal structure is similar to the Ni_3Al phase of the nickel-aluminum system. These particles are responsible for the age-hardening characteristics of these alloys, and their size, distribution, and coherency characteristics are generally considered to determine the hardness and matrix strength of the alloys. In the early stages of precipitation these particles are often only a few hundred Angstrom units in diameter. The grain boundary precipitates are usually carbides and nitrides such as $M_{23}C_6$, M_6C, Cr_7C_3, CbN, and TiN, depending on composition and aging treatment, and several investigations (324–329) indicate that these grain boundary phases markedly influence the long-time rupture strengths of the alloys. The presence of a "cellular" carbide structure of the type shown in Fig. 22 has been shown to result in very low rupture strengths (326).

The microstructures of other nonferrous alloys such as those of lead and tin (273), magnesium (58,336), molybdenum (337), silver (338), zirconium (339), and especially those of copper (279,340–344), aluminum (51,272,274–278,345–349), and titanium (7,280,349–354) have also been investigated by electron microscopy. The copper, aluminum, and titanium alloys are of particular interest because of their commercial importance and they are excellent subjects for electron microscopic investigations because they so often develop precipitates and transformation structures which cannot be resolved optically. An interesting example of this type is the omega phase which forms in binary alloys of titanium and elements such as chromium, iron, manganese, molybdenum, cobalt, nickel, and vanadium when these alloys are quenched from the beta field and subsequently aged in the temperature range from 700 to 900 F. The omega phase is apparently an intermediate step in the transformation of the matrix from the high-temperature body-centered cubic beta structure to the low-temperature hexagonal close packed alpha structure and occurs only in the presence of the beta phase, and then only in the form of extremely fine particles. It therefore cannot be resolved by optical microscopy, but it has been observed electron microscopically, using replica techniques, as shown in Fig. 23, and its structured characteristics have been determined by thin film techniques (351). Saulnier (350) has reviewed several earlier studies of nonferrous alloys and describes a number of other cases where new structures have been observed and new phases identified by electron microscopic techniques.

FIG. 23.—Particles of Omega Phase in an 8 Cr Titanium Alloy (× 32,000).

Electron microscopy has also made important contributions in studies of structures formed by plastic deformation of metals and alloys. Interest in this area appears to have originated with the discovery by Heidenreich and Shockley (355) that the slip "lines" which had been observed by optical microscopy in the surface of deformed aluminum were

actually lamellar bands of very closely spaced slip lines. A considerable number of investigations of slip structures have subsequently been reported. For the most part these have been carried out on pure metals or single-phase alloys with face-centered cubic structures (particularly aluminum, copper, and alpha brass) which were deformed at moderate rates by tensile stresses at room temperature. In general, it appears that the lamellar bands observed by Heidenreich and Shockley occur predominantly in the pure metals, while slip in the alpha brass occurs as individual, randomly distributed slip lines of large displacement (**356**). An additional "elementary slip" structure consisting of large numbers of very closely spaced slip lines of very small displacement has also been observed in the pure metals (**356,357**). Theoretical interpretations of these various fundamental slip structures have been developed and explanations have been offered for the characteristic differences observed between the pure metals and the alpha brass (**356**). These developments have been reviewed in part by Brown (**358**). Fourie and Wilsdorf (**359,360**) have described extensive qualitative and quantitative studies of the slip lines in alpha brass. Repeated observations on individual slip lines during the deformation process showed the lines to grow discontinuously but in definite steps suggestive of movement of bursts of dislocations or of the operation of cross slip mechanisms. Brandon and Nutting (**361**) have proposed modifications of the conventional theories of deformation of polycrystalline aggregates based on studies of slip lines on high-purity iron.

In addition to these investigations of relatively pure metals and single-phase alloys, a considerable number of investigations involving more complex alloy systems and more unusual deformation conditions have been described. These include, in part, investigations of the influence of radiation damage (**362**), temperature (**363**), and quench hardening (**364**) on the structure of slip bands in aluminum; the effect of ordering on slip structures in nickel-manganese alloys (**365**); the variation of slip structures with precipitation of secondary phases in 4 Cu aluminum alloy (**366,367**); and of slip band structures formed during fatigue loading (**368–376**). These various investigations have yielded a number of very interesting results. For example, in their studies of the 4 Cu aluminum alloy, Thomas and Nutting (**366**) found that the type of slip structure varied from individual randomly distributed slip lines in the early stages of aging to lamellar slip bands in the overaged alloy. In the overaged condition, the alloy contained partially coherent particles of the θ' phase and noncoherent particles of θ phase. When the slip bands encountered the partially coherent θ' particles they either stopped short of the particles and then continued on the other side, or passed through the particles causing them to be deformed. However, they always bent around the noncoherent θ particles and a cross slip mechanism was proposed to account for this. Koda and Takeyama (**367**) observed the deformation of the θ' particles both on the surface and in the interior of deformed specimens, and cite this as evidence that slip structures in the interior of the alloys are similar to those seen on the surface. The conclusions of Thomas and Nutting concerning the interaction of slip with precipitate particles have since been confirmed by thin film investigations (**257,289**).

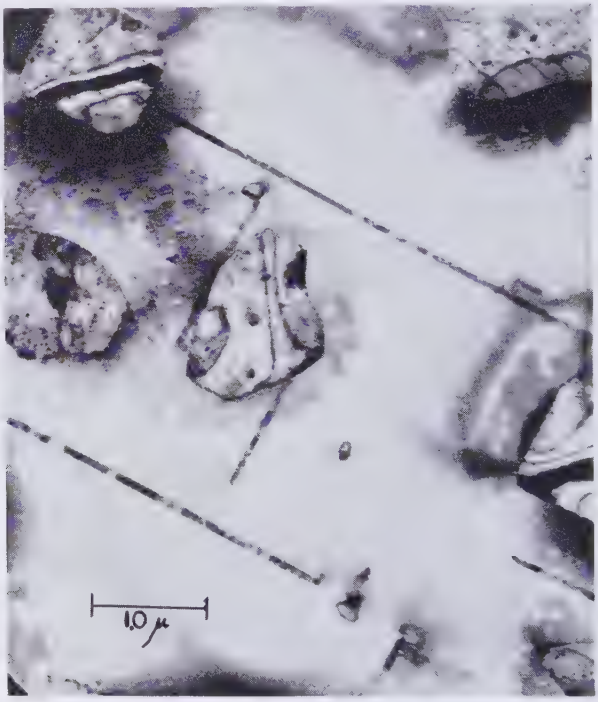
In the studies of fatigued metals it has been shown that cracks or fissures develop within the slip bands and eventually propagate to cause fracture. In an investigation to determine the stage in the tests at which the cracks first appear,

Hull (377) discovered that minute crevices often form in the slip bands before the tests run more than a few per cent of the estimated life of the specimens. The formation of these crevices is apparently related to the formation of extrusions (370,371) in the slip bands and is considered by Hull to be the first stage in the development of the cracks. In this connection it is interesting to note that Bendler (378) has reported that fatigue cracks in copper originate as numerous discontinuous fissures in abnormally distorted slip planes, and that Decker and Freeman (329) have observed that the rupture life of certain heat-resistant alloys in high-temperature creep tests depends on the rate of development of microcracks at the grain boundaries, while Young and Schwartz (379) have observed that the development of microcracks around hydride particles contributes to hydrogen embrittlement in zirconium alloys.

Considerable use has also been made of electron microscopic techniques in studying fracture surfaces (121,126,380–385), magnetic alloys (338,386–392), subgrain structures, etch pitting, recrystallization, polygonization, and related phenomena (359,360,393–399), and especially in studying various oxidation and corrosion processes (400–414). The use of fracture surfaces in exposing intergranular precipitate particles has been referred to above. Studies of fracture surfaces have also revealed characteristic structures of intergranular and transgranular fractures, and their relationships to precipitates, grain boundaries, and grain structure orientation. Studies of the magnetic alloys have revealed several cases in which submicroscopic structural units align in a particular direction when the alloy is cooled in a strong magnetic field, and evidence has been presented to support the view that the alignment of these units is associated with the permanent magnet characteristics of certain alloys. The observation of subgrain structures and dislocations has been of particular interest to metallurgists for many years, and much has recently been accomplished in this area through the development of better etching and replica techniques and the use of high-resolution microscopy. Work in this area will undoubtedly increase in the future because current theories suggest that in certain cases plastic deformation and creep are controlled by subgrain structures and dislocation interactions.

Combining electron microscopy with electron diffraction techniques provides a particularly effective means of investigating oxidation and corrosion processes, and a large number of studies of this kind have been described in the recent literature including studies of the corrosion of iron in water (400), the oxidation of aluminum at high temperatures (408), the passivity of lead and stainless steel (410–412), the reaction of H_2S with silver (409), and the passivation of iron by $NaNO_2$ (414). These investigations have contributed much to the general understanding of oxidation and corrosion processes, and have revealed several new features of these processes. For example, Gulbrandsen and associates (400–403) have discovered the formation of oxide crystals having unusual needle-like and plate-like shapes on iron and steels under certain corrosion conditions. The shapes and arrangements of the crystals are apparently influenced by the presence of water vapor and of certain ions in the corrosion medium as well as by the presence of precipitates and inclusions in the metals and the stress applied to the metal. Similar crystalline needles of silver sulfide have been observed in the reaction of H_2S with silver (409), and their formation has been related to the characteristics of the reaction rate. Numerous studies have been made of

the mechanisms and kinetics of oxidation and corrosion processes. In many cases the oxidation products appear to nucleate at rather widely separated sites on the surfaces of the metals and then to grow from these nuclei until the surface is covered, with considerable variation in structure and morphology at different stages in the process (404). Figure 24 shows small crystals of Cu_2O which formed at widely separated sites on the surface of a thin single crystal film of copper during the early stages of oxidation at 530 C in an oxygen atmosphere (0.9 μ Hg pressure). Recently Swann and Nutting (407) have obtained evidence indicating that the presence of stacking faults may influence corrosion rates and be an important factor in the fatigue and stress corrosion of metals.



Courtesy of R. Marcus, Department of Chemistry, The University of Michigan.

FIG. 24.—Small, Widely Separated Crystals of Cu_2O Formed on the Surface of a Thin Single Crystal Film of Copper During Exposure to Pure Oxygen at a Pressure of 0.9 μ Hg for 25 min at 530 C.

DEVELOPMENT OF ELECTRON OPTICAL METHODS FOR DIRECT OBSERVATION OF METAL SURFACES

Although transmission methods are being used extensively in metallurgical investigations and are contributing much new and useful metallographic information, they suffer from certain inherent limitations which severely restrict their applicability. In addition to being indirect, the replica methods are essentially static in character since the preparation of the replicas requires a considerable period of time during which test proce-

dures and heat treatments must be stopped. Furthermore, the replicas usually must be prepared at room temperature so that processes occurring at temperatures much different from this can be studied only if the specimens can be

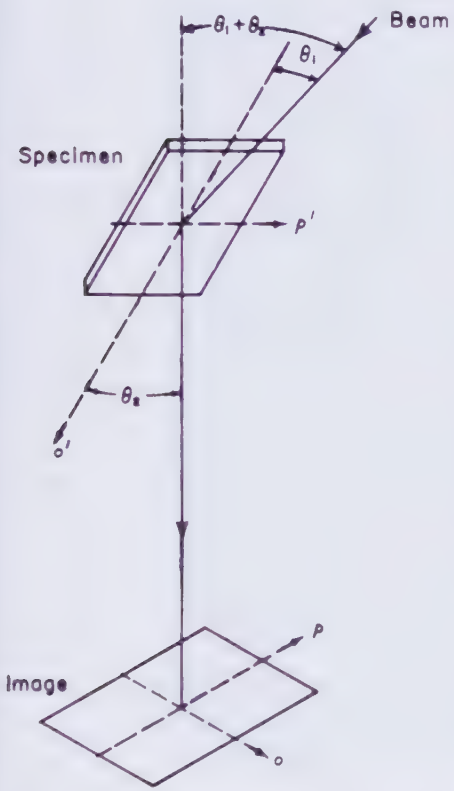


FIG. 25. Relation of the Orientation of the Specimen to the Electron Beam and the Image in Reflection Electron Microscopy.

brought to room temperature without significant structural changes by rapid quenching or heating. Transmission studies of thin films do permit direct observations to be made of microstructural features over a considerable range of temperatures and under some test conditions; however, it is not certain that observations made on such thin films can in all cases be taken as representative of those occurring in thick specimens of practical interest, and the difficulties involved in preparing thin films preclude their widespread use for many types of alloys at present. There is, therefore, considerable current interest in several special electron optical methods which are specifically designed to permit the direct observations of surfaces of thick solid specimens. These methods, which include reflection, scanning, emission, point-projection, and mirror microscopy, are described briefly in the following sections.

Reflection Microscopy:

In reflection microscopy the surface of the specimen is inclined at an angle to the axis of the objective-projector lens system and is illuminated directly with the electron beam. The image is then formed from the electrons which are scattered from the surface into the objective lens. This basic experimental arrangement is characterized by the angle of incidence of the illuminating radiation θ_1 and the angle of observation θ_2 as shown in Fig. 25.

Apparently the first experiments with reflection microscopy were performed by Ruska (415) in 1933 using a relatively simple electron optical system. In 1940 Ruska and Müller (416) reported work with a reflection microscope having a standard system of objective and projector lenses; however, the resolution obtained was inferior to that attainable by optical methods and the image intensity was so low that only relatively low magnifications could be used. These difficulties were attributed to the fact that very high angles of illumination and observation were used, with the total deflection of the electrons amounting to 90 deg (that is, $\theta_1 + \theta_2 = 90$ deg). Shortly thereafter, von Borries (417) re-

ported studies in which a resolution of the order of 500 Å was achieved using a modified Siemens electron microscope with small angles of illumination and observation (that is, $\theta_1 + \theta_2 \approx 8$ deg). Similar results were subsequently obtained by Raether and others (418–420) using a similar experimental arrangement. Although these results provided a considerable improvement in resolution over that attainable optically, general interest in reflection microscopy lapsed (apparently due to a number of factors, including the development of effective replica techniques for studying surface topology by transmission methods) until around 1950 when further investigations were undertaken in England (421–423), France (424), and Russia (425,426). An interesting review of this early work has been prepared by Cosslett (427). More recently a considerable number of studies in reflection microscopy have been reported (427–464), a majority of which have been concerned with examining the basic characteristics of the reflection method and with improving instrument design to achieve better resolution, greater con-

Courtesy of K. Ito, Japan Electron Optics Laboratory Co., Ltd.

FIG. 26.—Reflection Electron Micrographs of the Etched Surface of a Copper Alloy.
(*a*) $\theta_2 = 15$ deg, $M = 16{,}000\times$, $M/M_0 = 3.9$.
(*b*) $\theta_2 = 27$ deg, $M = 16{,}000\times$, $M/M_0 = 2.2$

venience and greater versatility of operation.

The fact that in reflection microscopy the surface of the specimen is observed at an oblique angle results in a foreshortening of the image which is not present in images formed from surface replicas observed by transmission at normal incidence. If M is the electronic magnification of the microscope in normal transmission microscopy, the foreshortening or distortion of the image in the direction o (Fig. 25) corresponding to the direction of observation of the surface o' is given by the ratio $M/M_o = \operatorname{cosec} \theta_2$. Here M_o may be considered as the effective magnification in the direction of observation. The effective magnification M_p in the direction p perpendicular to the direction of observation is equal to the electronic magnification (that is, $M_p = M$). Thus for an experimental arrangement of the type used by von Borries and in many subsequent investigations (417–430) where θ_2 is of the order of 6 deg, M/M_o is about 10. The effect of such a high degree of foreshortening on the appearance of the image is very marked as is shown in several interesting series of micrographs published by Menter (423), and often leads to difficulties in the interpretation of reflection micrographs. Consequently much effort has been devoted to reducing this distortion through the use of larger angles of observation. Work in this direction was begun by Menter (423) and Watts and associates (431,432) who used angles of observation as great as 12 deg. More recently Fert and associates (433–438), Ito (439), and Page (440,441) have employed angles of observation in the range from 20 to 30 deg. The effect of reducing foreshortening on the appearance of the micrograph is illustrated in Fig. 26. Fert et al (434–438) have shown that it is possible to reduce the foreshortening to any desired degree by placing a nonsymmetrical lens (both cylindrical and quadrapole lenses have been used) of adjustable strength and orientation below the projector lens of the microscope.

The resolution attainable in reflection microscopy is influenced by astigmatism, diffraction effects, and chromatic and spherical aberrations, as in transmission microscopy; however, because of the large amount of inelastic scattering which occurs when the electron beam strikes the solid surface, the electrons entering the objective lens have a sufficient range of energies to cause chromatic aberration to become the principal limiting factor. The dependence of resolution on ΔV, the average loss of energy by the electrons in the scattering process, is given by

$$R = C\alpha\Delta V/V \approx f\alpha\Delta V/V = r\Delta V/V$$

where:

R = the radius of the disk of confusion due to chromatic aberration,
α = the half-angle of the aperture of illumination,
r = the radius of the opening in the objective aperture,
V = the accelerating voltage, and
C = the chromatic aberration constant of the objective lens which is approximately equal to the focal length f in most cases.

Whereas ΔV amounts to only a few volts in normal transmission work, measurements by Haine and Hirst (421) and Kushnir et al (426) indicate that it is of the order of 100 v in reflection studies when the accelerating voltage is about 80 kv and θ_2 is in the range from 6 to 10 deg. Because of the wide angle of scattering of the electrons at the specimen surface, the aperture of the illumination forming the image is determined primarily by the limiting rays accepted by the objective aperture rather than by the divergence of the beam from the condenser lens as in transmission work.

Resolution is therefore also very much dependent on the size of the objective aperture. Menter (**423**) has estimated that if an aperture of optimum size were chosen, taking into account diffraction effects as well as spherical and chromatic aberrations, a resolution of the order of 50 Å should be possible. This aperture would be somewhat less than 10 μ in diameter, however, and would reduce the image intensity to such an extent that accurate focusing would not be possible. At present, the necessity for maintaining the image intensity at a level sufficient for visual focusing imposes a practical limit on the selection of the objective aperture which ultimately determines the resolution and the maximum electronic magnification that can be achieved.

There are, however, several factors in addition to the size of the objective aperture which are experimentally controllable and which contribute to determining the resolution attainable in reflection microscopy. From the equation above it will be evident that the focal length of the objective lens should be as small as possible, and in general this means that the specimen holder and the pole pieces of the objective lens must be designed to permit the specimen to be located as close as possible to the surface of the upper pole piece element. Resolution is also critically dependent on the accuracy with which the objective aperture is centered. This matter has been discussed in detail by Page (**440,441**) who also shows that by correctly adjusting the height of the aperture and the magnitudes and directions of the currents in the objective, intermediate, and projector lenses, the chromatic differences in magnification and rotation of the lens system can be minimized to obtain sharp focus over the widest possible field of view. These lens adjustments are particularly important when large angles of observation are used. A layer of carbonaceous contamination generally forms on the surface as a result of the decomposition of oil vapors by the electron beam (**442,443**). Fert and Dupouy (**71**) have shown that this carbonaceous layer may cause a considerable decrease in resolution in reflection work at high angles but that it can usually be eliminated by bombarding the surface with gas ions while it is under observation in the microscope. It should also be noted that because of the oblique observation of the surface, the effective resolution is not uniform in all directions in the micrographs and the value R referred to above applies only for the direction perpendicular to the direction of observation (that is, $R_p = R$). The effective resolution R_o in the direction of observation is generally poorer than this, and is given by $R_o = R \operatorname{cosec} \theta_2$. On the other hand, the effective resolution R_h for surface irregularities is much better than R. For an opaque asperity of height h, the shadow cast by the incident electron beam has a length $L = h \cot \theta_1$. The effective resolving power for the asperity is related to the resolving power for the shadow and can be shown to be $R_h = R \sin \theta_1 \operatorname{cosec} (\theta_1 + \theta_2)$. This value is somewhat dependent on the half-aperture angle of the incident beam (**436**), but the requirements in this regard do not impose serious limitation on the intensity of illumination.

The best resolution reported to date for low angles of observation is slightly less than 200 Å. This was achieved by Dupouy and Fert (**428**) using a 12.5 μ aperture with a lens having a focal length of 4 mm. More frequently, however, the resolution is in the range from 300 to 800 Å, since apertures ranging from 30 to 50 μ in diameter are used to achieve higher image intensities. Even so, exposures of the order of 20 sec are normal at magnifications of 2000× to 4000×. With high angles it is generally necessary to work with relatively larger apertures

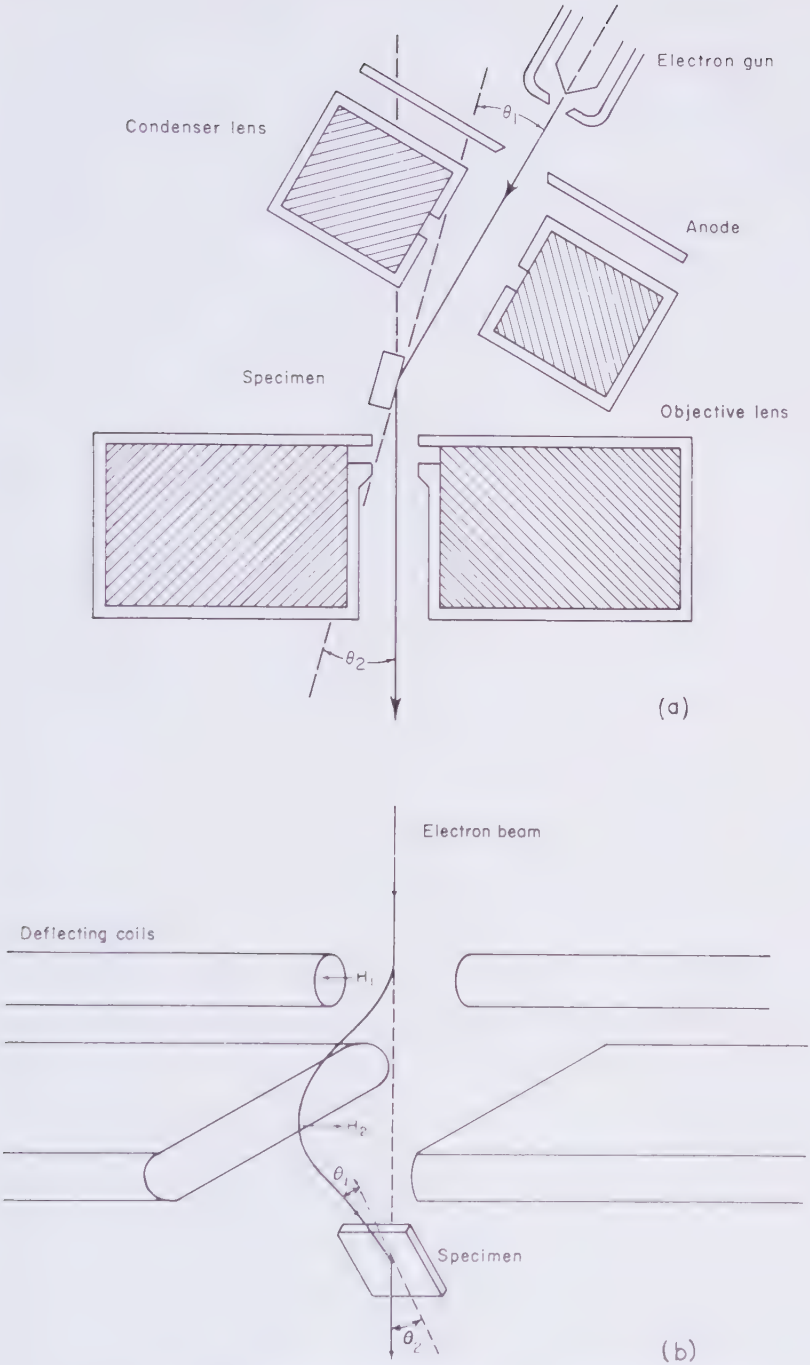


FIG. 27.—Methods of Illuminating the Specimen in Reflection Microscopy.
(*a*) Tilting the illuminating system.
(*b*) Deflecting the electron beam magnetically.

and lower magnifications since the intensity of scattering decreases as the total deviation of the electrons increases. From the early work of Ruska and von Borries (**415–417**) it was also thought that the value of $\Delta V/V$ increased rapidly with increasing deviations. Recent work by Fert and associates (**436–438**) and Page (**440,441**) show, however, that this is not the case for deviations up to 40 deg, and Fert, Marty, and Saporte have achieved a resolution of 350 Å over this entire range using a 30 μ aperture in a lens with a 3 mm focal length. It is interesting to compare the values of R_o and R_h with R for low-angle and high-angle reflection microscopy. Values calculated for typical cases are listed below:

	θ_1, deg	θ_2, deg	R, Å	R_o, Å	R_h, Å
Low angle	2	6	300	2900	75
High angle	2	25	500	1200	40

These values show that the resolving power of reflection microscopy for surface irregularities is well below 100 Å even when the resolving power for planar features is much less. Furthermore, there appears to be a definite over-all advantage to using high angles of observation, for in addition to giving micrographs which are easier to interpret, better values of R_o and R_h are obtained even when R is considerably poorer than when low angles are used.

While Fert and associates (**424,436–438**) and Cosslett and Jones (**444**) have employed instruments especially designed for reflection microscopy, most other workers have used standard transmission instruments adapted for reflection work by adding special specimen stages for manipulating the solid specimens (**436,445,446**) and modifying the beam path to permit the illumination of the specimen surfaces. This latter modification is usually accomplished by inserting a hollow wedge into the microscope column above the specimen chamber so that the electron gun and condenser lens are tilted at an appropriate angle with respect to the axis of the objective lens as shown in Fig. 27(*a*). This has the disadvantage of requiring disassembly of the microscope to convert from transmission to reflection microscopy, and so special devices permitting continuously adjustable tilt have been used in some cases (**421,436,445**). Ito and associates (**439,447, 448**) have developed a system of electromagnetic deflecting coils for the JEM electron microscopes which bends the electron beam in the manner shown in Fig. 27(*b*). This arrangement is very convenient for it allows continuous adjustment of the beam deviation up to 30 deg, and the microscope can be converted from transmission to reflection work simply by activating the deflecting coils. A system of this type was also used in some of the earlier work by Fert (**424**), and von Borries (**449**) has suggested the use of permanent magnets for the deflecting elements. Several other special devices have been developed for reflection microscopy, including specimen heaters (**450, 451**), stereoscopic attachments (**452**), electron spectrographs for determining the energy distribution in the scattered electrons (**437,453**), a specimen chamber for treating the specimen with a gas during observation (**448**), in addition to the corrective lens and ion gun developed by Fert (**436**) and referred to above.

The applications of reflection microscopy appear to be relatively limited in number and have been concerned mainly with nonmetallurgical topics such as studies of paper and pulp fibers (**431,432**), various textile fibers (**454–459**), surfaces of insects (**460**), oxide films (**461**), and the surfaces of diamonds (**462**). However, Jones (**463**) has reported on studies of metal surfaces at high temperatures, Thomas et al (**464**) have studied fatigue

deformation, and a number of excellent micrographs of metallurgical specimens have been published as illustrations of the results obtainable by the method (422,423,436–440,458). The limited application of reflection microscopy undoubtedly results from the facts that, to date, the method has been used in only a few laboratories and that it is, generally speaking, still in a state of development.

matic lenses to reduce chromatic aberration. Even in the present state of development, however, reflection microscopy would seem to have many features of potential advantage in metallurgical research. The magnification, depth of field, and general resolution are all much better than can be obtained by conventional optical microscopy, while the sensitivity to surface relief is comparable

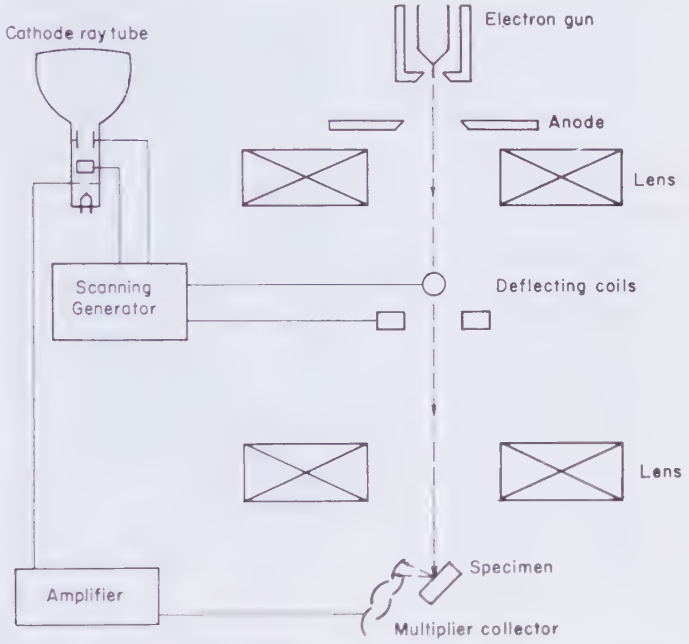


FIG. 28.—Schematic Diagram of the Scanning Electron Microscope.

It is undoubtedly true that there will be many general improvements in the method in the next few years. At present, the possibilities of improving the effective image intensity through the use of higher accelerating voltages, artificial focusing devices, image intensifiers, fine-grain high-speed photographic emulsions, and more sensitive fluorescent materials are under investigation as are the possibilities of improving resolution by employing electron velocity selectors, or achro-

to that attainable by optical interference or phase contrast methods. Only relatively minor modifications are required to adapt standard transmission instruments for reflection work (and this would seem to be a good use for older transmission instruments as they are replaced by newer and more versatile models), and there is a possibility of obtaining chemical analyses by microbeam X-ray fluorescence, although the selection of the area would not be as sharply defined

as in the more common version of this method where the angle of incidence is 90 deg.

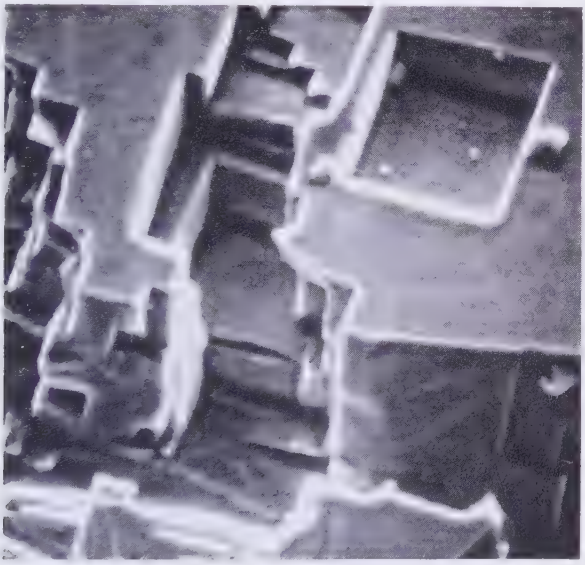
Scanning Microscopy:

The basic features of the scanning electron microscope are shown schematically in Fig. 28. In this instrument a beam of electrons is focused to a very fine spot which is caused to scan a small area of the specimen in a systematic pattern by means of a set of deflecting coils. Variations in the intensity of electrons scattered from the specimen are measured, amplified, and used to modulate the intensity of the beam in a cathode ray tube while the motion of the beam in the tube is synchronized with the movement of the electron spot over the specimen. Any variation in the intensity of scattering as the electron beam moves from point to point over the specimen produces a similar variation in intensity at the corresponding points on the screen of the cathode ray tube which, interestingly enough, generates an image of the specimen that is very similar in appearance to those obtained by other microscopic techniques. This principle was first investigated by Knoll (**465,466**) and subsequently by von Ardenne (**467,468**) and Zworykin, Hillier, and Snyder (**469,470**). However, many experimental difficulties were encountered in these early investigations due largely to the fact that adequate electronic equipment and detecting devices were not available, so that reasonably satisfactory results were first achieved by workers at the University of Cambridge using an instrument designed by McMullan (**471**) and subsequently improved by Smith and Oatley (**472,473**).

Two slightly different approaches to obtaining image contrast in scanning microscopy have been used in these investigations. The instrument of Zworykin, Hillier, and Snyder was designed to measure the intensity of low-energy (1 to 5 ev) secondary electrons emitted from the surface, and hence depended on variations in the secondary emission coefficient from point to point over the surface for image contrast. Based on these early studies, this method appeared to be of relatively limited applicability because the emission coefficient did not appear to vary enough to give a satisfactory signal-to-noise ratio for most types of materials. Furthermore, the necessity of using low-voltage (less than 1 kv) electrons to obtain a suitably high level of secondary emission introduced additional complications and experimental difficulties. In McMullan's instrument these difficulties were overcome by using an electron accelerating potential of about 20 kv with the specimen oriented so that the mean angle of incidence of illumination (θ_1) was in the range from 25 to 45 deg. Electrons scattered from the surface were collected on the first dynode of an electron multiplier which was maintained at a potential of about 500 v positive with respect to the surface and which was located as close as possible to the surface so as to collect electrons scattered through a solid angle of about 30 deg. Under these conditions, the electron scattering involved only a relatively small proportion of low-energy secondary emission but was predominantly inelastic in character and was strongly dependent on the local angle of incidence. Hence, as the beam scanned the surface, relatively large variations in scattered intensity resulted from point-to-point variations in the angle of incidence, and image formation was basically dependent on surface topology. Oatley and Smith (**473**) subsequently remodeled McMullan's instrument to use secondary electrons for image formation and achieved an improvement in image detail and contrast without loss in resolving power by em-

ploying more sensitive detectors and improved circuits. The successful use of secondary electrons has been reported more recently by other workers (474,479–482) so that present trends favor this method of image formation.

The resolution attainable in scanning microscopy is fundamentally dependent on the diameter of the scanning beam at the surface of the specimen. In the work at Cambridge, Smith and Oatley (472,473) report attaining resolutions in the range of 200 to 250 A at 20,000× using a beam of about 150 A in diameter, and they indicate that with further refinements in the optical system smaller beam diameters may be obtained and the resolution may be increased to below 100 Å. Since the electron beam is incident on the surface at an angle there is a decrease in effective resolution and a foreshortening of the image in the direction of observation such that $R_o = R \text{ cosec } \theta_1$ and $M\ M_o = \text{cosec } \theta_1$. It should be noted that there are at least two factors in addition to the beam diameter which strongly influence the resolution. The first of these is the resolving power of the cathode ray tube. To attain high-quality pictures, particularly at lower magnifications, the tube must have a very fine spot size, a fine-grain screen, and be capable of producing a high number of scanning lines per inch. With ordinary tubes maximum resolution can be achieved only at high magnifications; at low magnifications the resolution may become inferior to that of a light microscope. The second factor is the ability of the electrons to penetrate the surface. This makes it possible for them to pass through, rather than being scattered from, the peaks and edges of surface features and reduces the sharpness with



Courtesy of K. C. A. Smith and C. W. Oatley, Engineering Laboratory, University of Cambridge.

FIG. 29. Micrograph of the Surface of a Heavily Etched Aluminum Specimen Taken with the Scanning Electron Microscope.

$\theta = 45$ deg. $M = 3000 \times$ $M/M_o = 1.4$

which the features are delineated. This phenomenon is very difficult to eliminate and may ultimately become the limiting factor in determining the resolution of scanning microscopy.

It is perhaps of interest to compare scanning microscopy with reflection microscopy since both methods appear to perform somewhat the same function in relation to other types of microscopy. In their present states of development and under normal conditions of operation, the resolutions attainable by both methods appear to be about the same and to fall in the range from 400 to 1000 Å; however, the fact that much higher angles of incidence are normally used in scanning microscopy than in reflection microscopy causes several differences in the characteristics of the two methods which are important in determining their relative areas of application. One of the advantages noted for reflection microscopy was the exceptionally high resolution for surface irregularities which is achieved through the use of low angles of illumination. In scanning microscopy where much higher angles of illumination are used the sensitivity to surface relief is very much less, and Page (440) has estimated that it is actually no better than the resolution in the direction perpendicular to that of observation (that is, $R_h = R_p = R$). The use of the low angles of incidence has a disadvantage, however, in that the larger asperities on the surface may cast long shadows, and areas of the surface in these shadows and in depressions receive no illumination and are obscured from view. Reflection microscopy is thus restricted to the examination of relatively smooth surfaces. On the other hand, with the high angles of illumination used in scanning microscopy the shadows are short, and even relatively deep depressions are fairly well illuminated so that very irregular surfaces can be examined. This is illustrated by the micrograph of the heavily etched aluminum surface shown in Fig. 29. Virtually none of the structural detail which can be seen in the etch pits in this micrograph would be revealed by reflection microscopy. Studies of various paper pulps and fibers by Atack and Smith (475) and observation on other fibers and biological specimens by Smith and Oatley (472) and Thornley (480) indicate that the incident beam intensity in the scanning microscope can be reduced to the point where specimen damage and contamination due to bombardment by the incident electrons are virtually eliminated. This is apparently made possible by a number of factors including the relatively efficient system used in collecting the scattered electrons, the subsequent amplification of the signal to form the final image, the very small diameter of the beam spot, and the fact that the beam spot is continually moving over the surface of the specimen. As a final point in this comparison it might be noted that the scanning microscope is inherently more complex than the reflection microscope and at present is considerably more difficult to obtain since one cannot be produced by making simple modification in a transmission instrument. The advantages and potentialities of scanning microscopy are such, however, that it seems almost certain that commercial instruments will become available in the near future.

In the metallurgical field, scanning microscopy would appear to offer little advantage over conventional replica techniques for routine studies of metallurgical structures. However, it could be used to definite advantage for a number of other purposes such as examining fractures, rough castings, and surfaces which are heavily etched, corroded, or abraded; determining the morphology of precipitate particles extracted from metal specimens; studying the surface charac-

teristics of abrasives, catalysts, fine wires, and metal powders; and studying the structures of porous materials such as ferrites and sintered metal products. By equipping the instrument with a suitable hot stage it would be possible to observe directly surfaces of metal specimens during deformation at elevated temperatures and to follow physical and chemical changes such as sintering, sublimation, and thermal decomposition. Some work of this nature has already been reported by Davoine (474) who has studied the deformation of metal specimens, and by McAuslan and Smith (476) who have observed the thermal decomposition of single crystals of certain explosive compounds. Some applications of scanning microscopy to transistor research have also been reported (473,477, 478) which have demonstrated the usefulness of the method in observing the location of p-n junctions in silicon transistors. The work of Cosslett and Duncumb (479–481) and Castaing and Slodzian (482) has also shown that it is possible to combine X-ray fluorescence analyses with scanning microscopy. This combination is particularly advantageous for analyzing inclusions and precipitates in metallurgical specimens when a long-persistence cathode ray tube is used, since the surface can be observed by scanning microscopy and then the electron beam can be accurately located over any point on the surface for analysis, and this feature is incorporated into most present microprobe analyzers.

Emission Microscopy:

The emission electron microscope occupies a preeminent place in the history of electron microscopy, for the first successful electron microscope was an instrument of this type described by Brüche and Johannason in 1932 (483) shortly before the first transmission microscope was described by Knoll and Ruska (484). The principle of the emission microscope is quite simple: the specimen is excited by heat, ion bombardment, or irradiation, and the electrons emitted from its surface are acted upon by an appropriate lens system to form an image of the surface. In practice, however, there are several factors which act to limit the resolution and field of application of the instrument and which undoubtedly are responsible for the fact that it has not achieved the popularity of the transmission microscope.

Under normal conditions of excitation, the majority of the electrons emitted from the surface of a solid specimen have energies of less than 2 ev. To use these electrons effectively for image formation in a practical vacuum system it is necessary to accelerate them to energies of several thousand electron volts. Since they leave the surface in random directions and with a distribution of energies, they enter the lens system with a considerable range of velocities and with a rather wide maximum angle of divergence from the optic axis, and chromatic aberration becomes the major factor controlling the resolution. The first thorough theoretical study of emission microscopy is generally attributed to Recknagel (485,486) who showed that to a first approximation the limiting resolution is given by $R = Cv/E$, where v is the "volt equivalent" of the average energy of the emitted electrons, E is field strength of the accelerating field, and C is a constant which is usually taken as having a value of unity. Since E cannot exceed about 150 kv per cm without electrical discharge, and v usually is in the range from 0.1 to 0.2 v, the theoretical limiting resolution for an emission microscope is of the order of 50 Å (487). In practice, such factors as instrument instabilities and distortions in the accelerating field due to local microscopic

surface irregularities limit the resolution to values considerably poorer than this.

Although a number of investigations using emission microscopy were undertaken in the 1930's (488–492), the magnifications and resolutions achieved were seldom significantly better than could be obtained by optical microscopy. In 1942, following Recknagel's work, several instruments were designed which demonstrated resolutions below 1500 Å (493–495), and one constructed by Mecklenburg (496) achieved a resolution of 400 Å. It appears, however, that these instruments were not used in any systematic studies of solid surfaces, and that virtually no further work was done in the field until the early 1950's. Since then interest in the uses of the method has steadily increased, and considerable progress has been made in improving the design of the instruments to provide better resolution, higher magnification, and greater convenience and versatility of performance. Recently a resolution of 250 Å has been reported with reasonable expectations of further improvements (497,498). Some of the recent improvements in the optics of the emission microscope are described briefly below, followed by a review of the characteristics and applications of the method.

Most of the emission microscopes built to date have used an immersion electrostatic lens of the type shown in Fig. 30 as the basic optical element. This is a very convenient arrangement since it provides a means of accelerating the emitted electrons and at the same time produces a magnified image of the surface. In the early instruments this type of lens was used alone, but in the later ones it was usually combined with an electrostatic projector lens as shown in Fig. 30 to achieve higher magnifications. A number of studies of the optical characteristics of this type of lens were carried out (for example, 487,499), and several instruments that were practical to use and capable of resolutions better than 1000 Å were built with this type of lens system (500–502). Subsequently Mollenstedt (503) and Bayh (504) showed that the resolution can be further improved

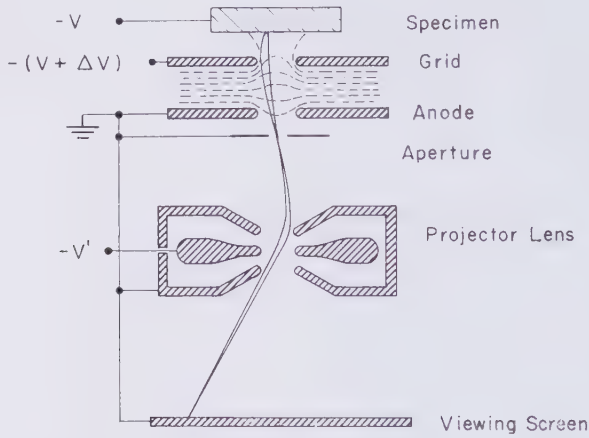
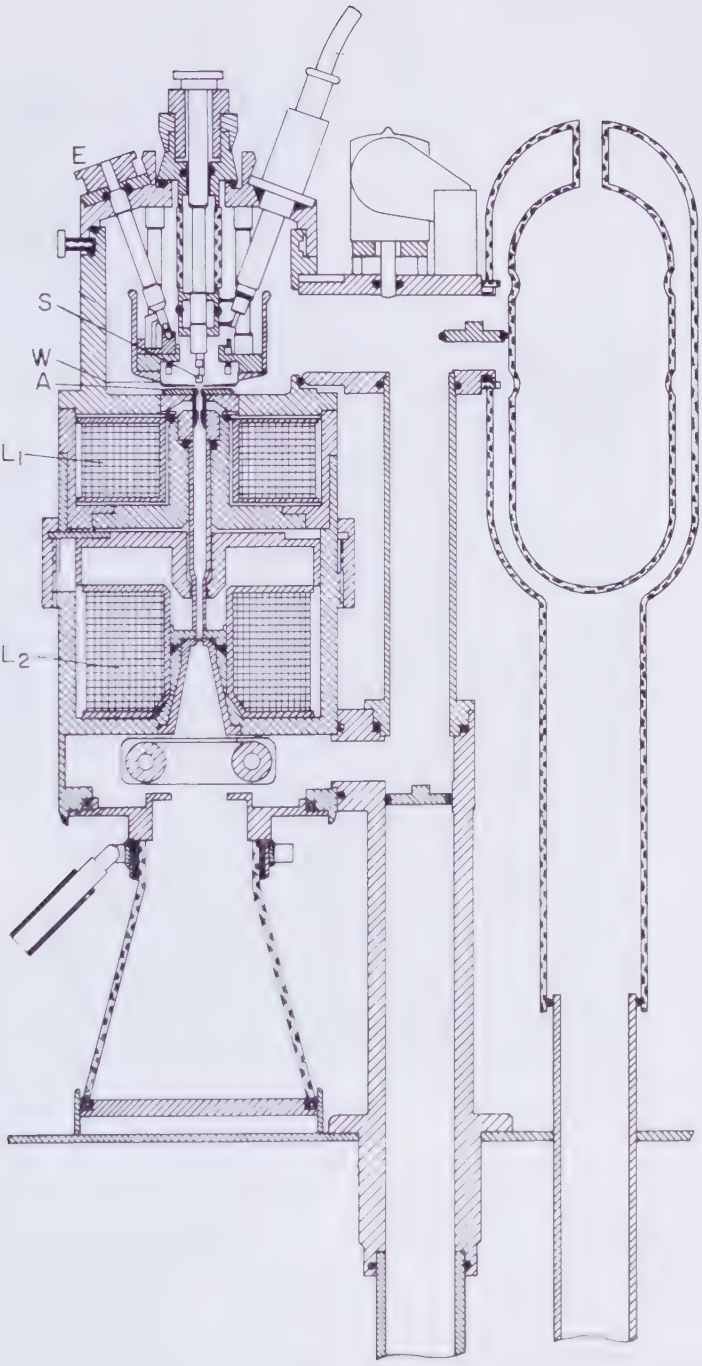


FIG. 30.—Schematic Diagram of an Optical System for an Emission Microscope Using an Electrostatic Immersion Objective Lens and an Electrostatic Projector Lens.

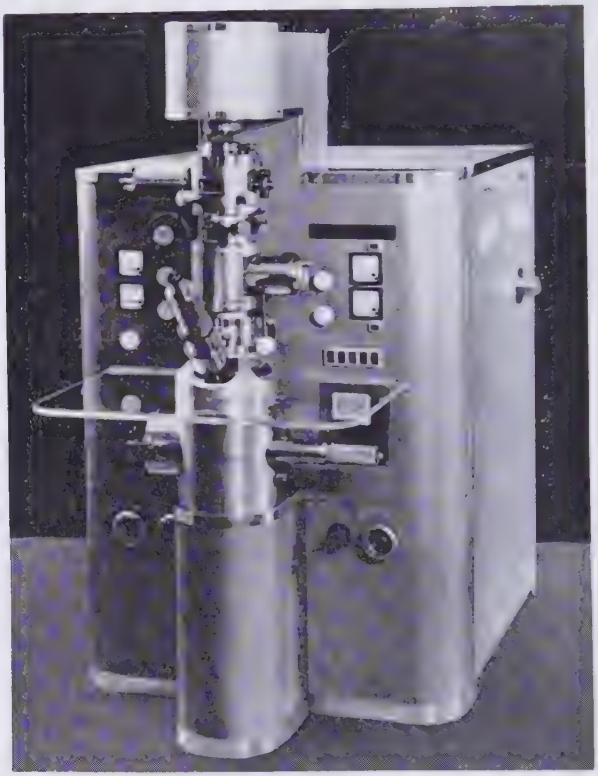


Courtesy of G. Baas, The Philips Research Laboratories, Eindhoven.

FIG. 31. Cross-Sectional Drawing of the Philips Thermionic Emission Electron Microscope Showing an Optical System Using Magnetic Lenses.

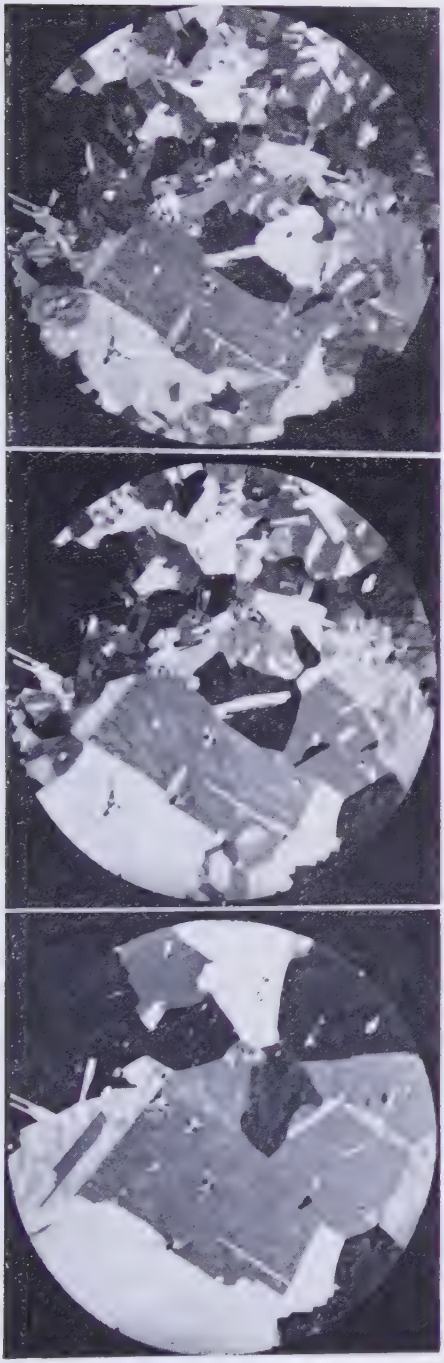
S = specimen, W = Wehnelt electrode, A = anode, L_1 and L_2 = magnetic lenses, E = evaporator for activator elements.

to about 400 Å by accurately centering a small aperture (approximately 15 μ in diameter) on the optic axis in the back focal plane of the objective lens. The present trend, however, appears to be toward the use of a simplified type of electrostatic lens in conjunction with a specially designed magnetic lens to replace the classical electrostatic immersion objective, the advantage being that the specimen can be brought closer to the anode and higher field strengths obtained. Magnetic lenses were first used in an emission microscope in 1942 by Kinder (494). In 1954 the Philips Co. introduced a commercial instrument developed by Rathenau and Baas (505) with two magnetic projector lenses and an immersion objective. As shown in Fig. 31, the anode of the objective of this instrument rests on the top pole piece of the first projector while the grid or Wehnelt electrode is constructed somewhat like that of the usual electron gun and operates with a fixed bias. The magnification is variable from 150 to 3000× by raising and lowering the specimen in the Wehnelt electrode and by adjusting the magnetic lenses. The resolving power is of the order of 1000 Å. This instrument is similar in over-all appearance to the Philips EM-75 transmission microscope (Fig. 3). Fert and Simon (497,498) have recently described a specially designed



Courtesy of Trüb-Täuber, Zurich, and the New England Scientific Instruments Co.

FIG. 32.—The Trüb-Täuber Model KE-1 Emission Electron Microscope.



magnetic objective lens in which the grid electrode is effectively eliminated, permitting field strengths up to 150 kv per cm to be achieved. With an aperture of optimum size properly located at the back focal plane of this lens, resolutions of 250 Å have been attained. Mollenstedt and Düker (506) have also developed an emission instrument using magnetic lenses, and the Trüb, Täuber Co. has produced a commercial model (Fig. 32) based on this design which has a resolution of 500 to 600 Å.

The characteristics of emission microscopy are somewhat dependent on the method used in bringing about the emission of electrons from the surface of the specimen. The method most commonly employed in the past is the thermal or thermionic emission method in which the specimen is heated to a temperature where spontaneous emission occurs. Here image contrast arises from abrupt variations in surface contour which produce inhomogeneities in the accelerating electric field, and from variations in the emissivity of different areas of the surface. In practice the emissivity of most metals is quite low in the temperature range of interest and varies only slightly over the surface, even when different phases are present; therefore, it is common practice to coat the surfaces of specimens with very thin layers of activators such as barium, strontium, or cesium. These materials lower the work function of the surface and greatly increase image intensity. In addition, their adsorption on the surface varies markedly for different phases and even for different grains of the same phase, depending on the composition, structure, and crystal-

Courtesy of S. R. Rouze, General Motors Research Lab

(*a*) 1800 F. (*b*) 1850 F. (*c*) 1900 F.

FIG. 33. Sequence of Thermionic Emission Micrographs Showing Grain Growth in SAE 1080 Steel (× 310).

lographic orientation in the surface, so that image contrast is also enhanced. The preparation and application of activators and the mechanism of the activation process have been discussed in some detail by Heidenreich (501). The working temperature range varies for different activators depending on their volatility and surface mobility: for barium it is from 900 to 1200 C and for cesium, from 500 to 750 C. The Philips emission microscope, which is of the thermionic type, contains apparatus for evaporating three different activators on the surface of the specimen during observation to permit as wide a temperature range as possible to be used. Figure 33 is a series of thermal emission micrographs showing grain growth in a eutectoid steel taken with this instrument.

It is also possible to induce electron emission by bombarding the specimen surface with a beam of positive ions. Although this method was used by Mahl (492) as early as 1938, its present popularity is due largely to the work of Mollenstedt and associates (502–504,506–511) who have made extensive studies of the energy distribution of the emitted electrons, the mechanisms of contrast, and factors controlling resolution in the ion-emission microscope. In Mollenstedt's instruments, the ion gun operates at a potential which is variable from 15 to 40 kv and produces a maximum ion beam current of the order of 1 μa. The ion beam is directed at the surface at an angle which can be varied from 0 to 20 deg. Image contrast arises primarily from shadow effects produced by the low angle of incidence of the ion beam, since emission occurs only from those areas of the surface that are struck by the beam. The micrographs are thus somewhat similar in appearance to reflection and scanning micrographs except that there is no foreshortening. Some contrast may also arise from variations in the secondary emission coefficient, although this is often obscured by contamination of the surface with a carbonaceous layer due to the ion bombardment. Mollenstedt reports, however, that this difficulty can be largely eliminated by heating the specimen to 200 C. The ion gun may also produce an etching of the surface, particularly if long exposures and high ion currents are used. The new Trüb, Täuber microscope (Fig. 32) is an ion-emission instrument. Bartz (512) and Bethage and associates (513) have also described recent models of ion-emission microscopes.

Several other emission microscopic techniques have also been investigated. Brüche, Mahl, and Pohl (490–492), and more recently Mollenstedt (511) and Gauzit, Huguenin, and Septier (500,514), have achieved considerable success in using the photoemission principle. This method offers the advantage of reducing the damage to the surfaces being examined. The indications are that resolutions comparable to those of other emission methods can be attained, although problems have arisen due to surface contamination, and the level of intensity is frequently not as high as might be desired. Bernard and Goutte (515) have described a method of obtaining images of metal surfaces bombarded with H^- ions, while Stuhmer (516) and Shapland, Feather, and Brown (517) have described microscopes that employ particles emitted from radioactive specimens for image formation. The resolution of these latter instruments is of the order of 1 μ, which is an improvement over ordinary autoradiographic techniques. Arnal (518) has also described an instrument which combines emission microscopy with reflection electron diffraction.

The principal application of emission microscopy in the past has been in studies of phase transformation and grain growth at high temperatures.

Brüche and Burgers and their associates (488–489) studied the $\alpha \rightarrow \gamma$ transformation in iron and the transformation of beta zirconium to the alpha form in some of the earliest work that was undertaken with emission microscopy. Since 1950 a number of investigations of similar nature have been reported (519–527), including investigations of grain boundary migration, recrystallization phenomena, grain growth, and phase transformations in steels and titanium. The emission microscope is particularly effective for such work since the surface of the specimen can be observed directly while the temperature is raised or lowered, and it is common practice to photograph the structural changes with a movie camera so that they can later be viewed and studied in detail. Because of the limitations in resolution and magnification, these past studies have been concerned only with the microstructural changes of the grosser kind. However, as a result of the recent improvements in instrumentation, the resolution now attainable by emission methods is nearly as good as that which is achieved in many of the ordinary studies by replica techniques, and it should be possible to use emission microscopy to study precipitation processes and other fine microstructural changes in the near future. The development of the photo- and ion-emission techniques in which the emission coefficients are fairly sensitive to compositional differences also suggests the possibility of studying diffusion processes by emission microscopy.

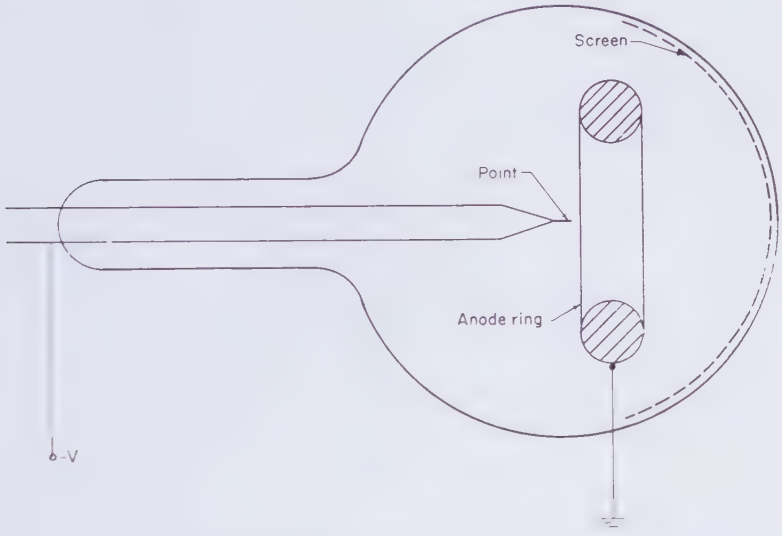
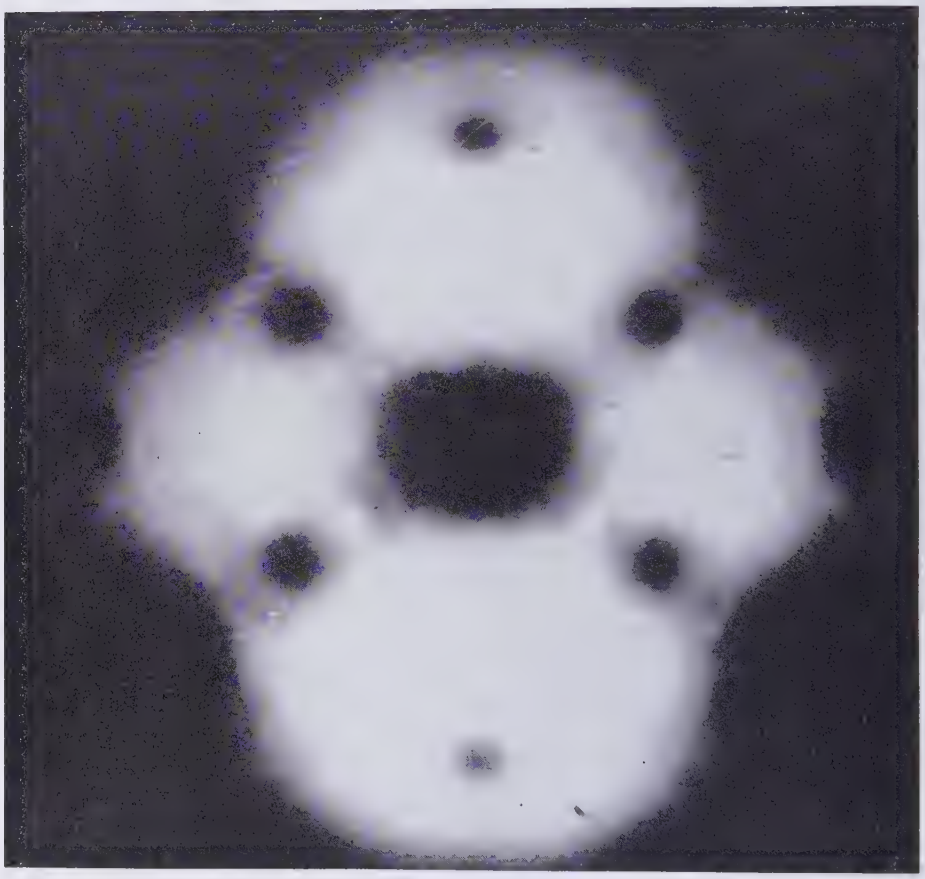


FIG. 34.—Schematic Diagram of the Field Emission Microscope.

Point-Projection Microscopy:

Point-projection microscopy has attracted considerable attention recently because it is capable of providing higher electronic magnifications and better resolution than any other microscopic technique presently available. The simplest type of point-projection microscope, which is more commonly known as the field-emission microscope, was developed by Müller (528) about 1936. The basic construction of this instrument

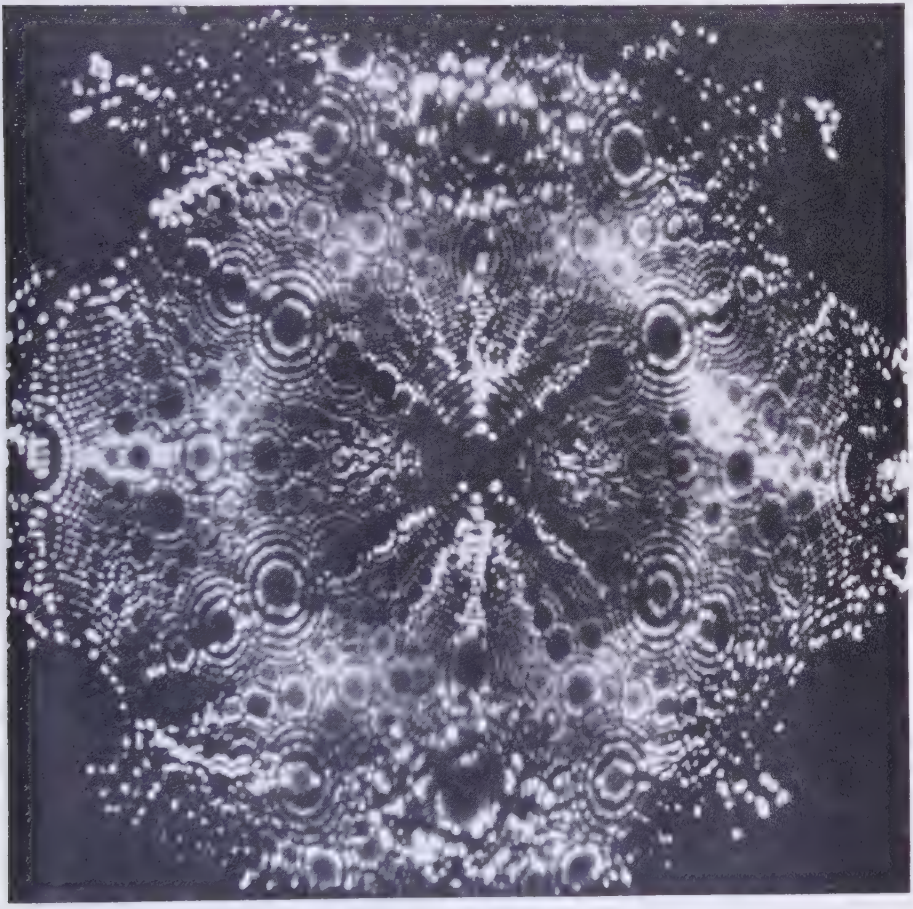
is shown schematically in Fig. 34. The point, which forms the cathode of the instrument, is prepared by special etching techniques so that it has a smooth hemispherical tip with a radius of the order of 1000 A. As shown, the point is located in the proximity of an anode ring at the center of curvature of an evacuated tube which is partially coated with a fluorescent material to form a viewing screen. By applying a potential of a few thousand volts to the anode ring, a field strength of the order of 5×10^6 v per cm is produced at the tip. This is sufficient to overcome the potential barrier at the surface of the metal and to draw electrons from the tip. Ideally, all electrons emitted from a given point on the surface of the tip would travel in a straight line perpendicular to the surface and form a corresponding spot on the fluorescent screen. In practice, the electrons have a small component of velocity tangential to the surface so that the idealized point is expanded into a disk. The resolving power of the instrument is limited by the magnitude of the tangential velocity and



Courtesy of E. W. Müller, Physics Department, Pennsylvania State University.
(*a*) Field emission micrograph.

FIG. 35.—Point Projection Micrographs of Tungsten Tips.

is given by $d = 2r\sqrt{v/V}$, where d is the diameter of the disk of confusion at the tip, r is the radius of the tip, v is the "volt equivalent" of the tangential velocity component of the electrons, and V is the potential difference between the tip and the anode ring expressed in volts (529). The magnification depends on the radius of the tip relative to that of the tube and is given by $M = D/r$, where D is the distance from the tip to the fluorescent screen. Müller (529) has reported attaining a resolution of 12 Å using a tip with a radius of 110 Å and an anode potential of 540 v. More usually tips ranging from 500 to 1000 Å in radius are used with potentials of from 2000 to 5000 v, giving resolutions in the range from 15 to 20 Å and magnifications from 500,000× to 2,000,000× (530).



(b) Field ion micrograph

FIG. 35. *Continued*

The emission current is related to the work function ϕ of the surface and the electric field strength E by the Fowler-Nordheim expression: $I \propto (E^2/\phi) \exp(-\phi^{3/2}/E)$. Contrast thus arises from variations in ϕ for different crystallographic planes and from local changes in E due to surface irregularities (which

may be of atomic dimensions). Although the magnifications attainable are adequate for resolving individual atoms, the limitations on resolution are such that field-emission micrographs usually show only the different crystallographic faces

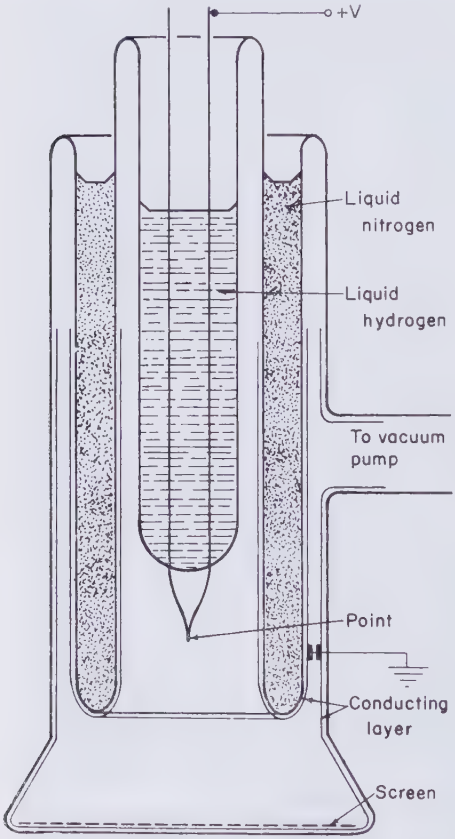


FIG. 36.—Schematic Diagram of the Field Ion Microscope.

exposed in the surface of the tip, as shown in Fig. 35(*a*).

More recently Müller (531–535) has developed an improved type of point-projection microscope, known as the field-ion microscope, which has a resolving power great enough to show individual atom sites in the surface of the tip. In this instrument, depicted schematically in Fig. 36, the tip is cooled to very low temperatures with liquid helium or liquid hydrogen and a positive potential is applied to it in the presence of helium, neon, or hydrogen gas at a pressure of 10^{-4} to 10^{-3} mm Hg. Under these conditions, large numbers of the gas molecules condense on the surface of the tip where they are cooled and lose most of their kinetic energy. As they re-evaporate from the surface, ionization occurs at a distance of about 5 Å from the surface and the ions formed are accelerated to the screen by the applied potential. Considered on an atomic scale, the surface of the rounded metal tip consists of a succession of step-like irregularities which are formed by the intersections of the atom planes with the surface. Since the electric field strength is greatest in the neighborhood of protrusions from the surface, ionization occurs most readily at the corners of these planes and above the sites of other prominent or protruding atoms. The picture produced on the screen thus consists of a pattern of bright spots of the type shown in Fig. 35(*b*), which are images of these prominent atoms. The relationship between this type of micrograph and the structure of the surface of the tip has been very clearly illustrated by drawings and pictures of models by Müller (532) and by Drechsler and Wolf (536).

The indications are that the resolving power of the field-ion microscope is determined primarily by the average wavelength of the gas molecules at the instant of ionization. This can be calculated approximately from the expression $\lambda = h/\sqrt{3mkT}$ based on the kinetic theory and the deBroglie relationship, and for a typical case of helium atoms varies from 3 to 6 Å for temperatures ranging from 20 to 4 K. Thus, the resolution of the instrument can be controlled in practice by varying the temperature

of the point and by using ions of different masses. The best experimental resolution reported to date is about 2.7 A, and this was achieved using helium ions and very fine tips cooled with liquid hydrogen (533–535). Since these are not the best conceivable conditions, it is possible that even better resolution can be achieved.

Point-projection microscopy involves many limitations and experimental difficulties due to the necessity of working with specimens in the form of fine metal

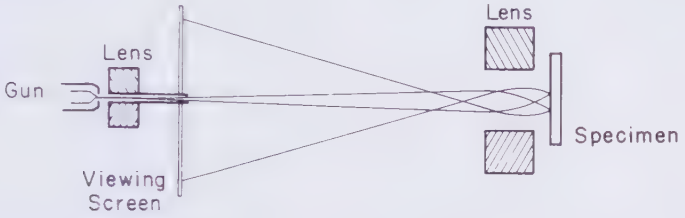


FIG. 37.—Schematic Diagram of the Optical System of Mayer's Electron Mirror Microscope.

Courtesy of L. Mayer, General Mills, Inc.

FIG. 38.—Electron Mirror Micrograph Showing the Magnetic Pattern of an MnBi Film.

points, and therefore is not well suited for general metallographic studies. Nonetheless, the high resolutions and magnifications attainable make it uniquely advantageous for many purposes. During recent years a surprising number of practical applications have been made of field-emission microscopy (537–552), including studies of: the polarization of atoms and molecules; lattice constants and atomic radii in metal crystals; phase transformations in titanium, molybdenum, and cobalt; the adsorption and mobility of atoms on metal surfaces; the work functions of different faces of single crystals; the chemisorption of various gases on metals; the formation of carbides; the shapes of large molecules; and the determination of the directions of screw dislocations. With field-ion microscopy it is possible to observe atom arrangements associated with twinning, dislocation, and crystal imperfections due to radiation damage, and it has even been possible to observe the movement of dislocations in the metal tip under the influence of the stresses exerted by the extremely high electrical field. The recent introduction of a commercial model of the field ion microscope by the Central Scientific Co. will undoubtedly stimulate the use of point-projection microscopy in research on the structures and properties of metals.

Mirror Microscopy:

In 1955–1956, Bartz, Weissenberg, and Wiskott (553,554) and Mayer (555) described a new type of electron microscope in which the specimen is caused to function as an electron mirror by maintaining it at a potential a few tenths of a volt negative with respect to the electron source. Electrons directed toward the specimen are reflected in the electric field just above its surface and pass through an arrangement of electron lenses or magnetic fields to form a magnified image of the electric field on the viewing screen as shown in Fig. 37. Variations in the contour of the surface or in its electrical or magnetic properties produce irregularities in the reflecting field and hence appear in the electron image. The method has been used by Bartz and Weissenberg (556) in studies of transistor junctions, and by Mayer (557–561) in studies of magnetic structures of various materials. Figure 38 is an electron mirror micrograph showing the magnetic characteristics of the surface of a MnBi film. The dark shadow extending from the center of the micrograph to the right is an image of the exit tube of the electron gun which extends through the viewing screen in Mayer's instrument. In most of this work to date, relatively low magnifications (less than 1500×) have been used, and the resolution has been of the order of a few tenths of a micron; however, the electron optical principles of the method have not been extensively investigated, and the indications are that with more refined optical systems it should be possible to achieve resolutions and magnifications comparable to those of emission microscopy. The sensitivity of this method to electrical and magnetic characteristics of the surface as well as to normal structural details, and the fact that the surface is not actually struck by the illuminating electrons, are features which make it appear promising for work in a number of areas where other methods are not applicable.

SUMMARY

Rapid progress has been made in nearly all phases of electron microscopy during the past few years. In preparing this review, an attempt has been made to indicate those developments which are of particular interest in metallurgical research; consequently, many important developments in electron optics, instru-

mentation, and in applications of electron microscopy to studies of plastics, minerals, and biological materials have not been discussed. References to the original literature and to many review articles on these subjects can be found in special bibliographies and literature surveys of electron microscopy (562–568) and in the various abstract journals (especially the *Bulletin signalétique*, Centre National de la Recherche Scientifique, Paris, which has sections devoted to electron optics and to structural studies by electron methods).

Concerning the topics discussed here, it seems particularly important to note that in addition to the great increase in the use of familiar transmission techniques in metallurgical research, considerable progress has been made in developing several other electron microscopic techniques which appear to offer definite advantages for many metallurgical investigations. These latter methods have been described in some detail with the hope of stimulating more work on their development and use in metallurgical laboratories in the United States. Discussions of these methods can also be found in other review articles (12,17,25, 32,427,429,569–573).

The accompanying references include most of the articles which describe fundamental developments in instrumentation and recent innovations in techniques. However, no attempt has been made to include all recent articles describing applications of electron microscopy in metallurgical research.

Acknowledgment:

The author would like to express his sincere appreciation to the numerous persons and organizations that have contributed illustrations of their instruments and research results or otherwise assisted in the preparation of this article.

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A STUDY OF THE MICROSTRUCTURE OF PRECIPITATION HARDENING STAINLESS STEEL SHEET*

By James C. Wilkins[1] and R. E. Pence[2]

Task Group E of Subcommittee XI on the Electron Microstructure of Metals of ASTM Committee E-4 on Metallography is in the midst of thin-section studies of various alloys by direct transmission electron microscopy. The precipitation hardening stainless steels are included in this program for the purpose of observing age hardening phenomena.

Investigations of the age hardening mechanism in 17-7 PH and PH 15-7 Mo stainless steels have been conducted at the Armco Research Center using the replication technique. These studies should serve as a background for the work now in progress using the thin foil technique.

The specified ranges in chemical composition for the steel sheets investigated are given in Table I.

The PH 15-7 Mo stainless steel is similar in many respects to 17-7 PH. However, molybdenum is added to increase its strength properties at temperatures up to 1000 F.

The precipitation hardening stainless steels are easily formed in the annealed condition and may then be hardened to high strength levels by the heat treatments outlined in Table II.

The hardnesses obtained by these treatments are:

Condition	Rockwell Hardness
A	B 88
T	C 30
TH 1050	C 44
R-100	C 38
RH 950	C 48

The marked increases in hardness resulting from the 950 F and 1050 F treatments indicate the degree of hardenability of the precipitation hardening stainless steels.

Specimen Preparation and Examination Using the Optical Microscope

Micro specimens were prepared from 0.050 in. thick commercial sheets. All specimens were taken in the longitudinal direction. They were final polished using an electropolishing solution of 78 parts perchloric acid, 120 parts water, 700 parts ethanol, and 100 parts of glycerin. They were first examined using optical microscopy. The etchants used for annealed precipitation hardening stainless steels were:

Reagent No. 1 . . . . 2 parts nitric acid, 1 part acetic acid, 10 sec, electrolytically

Reagent No. 2 . . . . . 10 per cent oxalic acid (10 g oxalic acid in 100 ml H_2O), 15 sec, electrolytically

(Reagent No. 2 is used to remove stains from reagent No. 1)

These steels in condition A (annealed at 1950 F) contain stringers of ferrite in a matrix of austenite (Fig. 1). The

* Presented at a Technical Session during the Sixty-fourth Annual Meeting of the Society, June 26, 1961.

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ferrite content will vary from 5 to 15 per cent depending on the chemical balance. The grain size of the austenite matrix is normally very small—ASTM grain size 10 or finer.

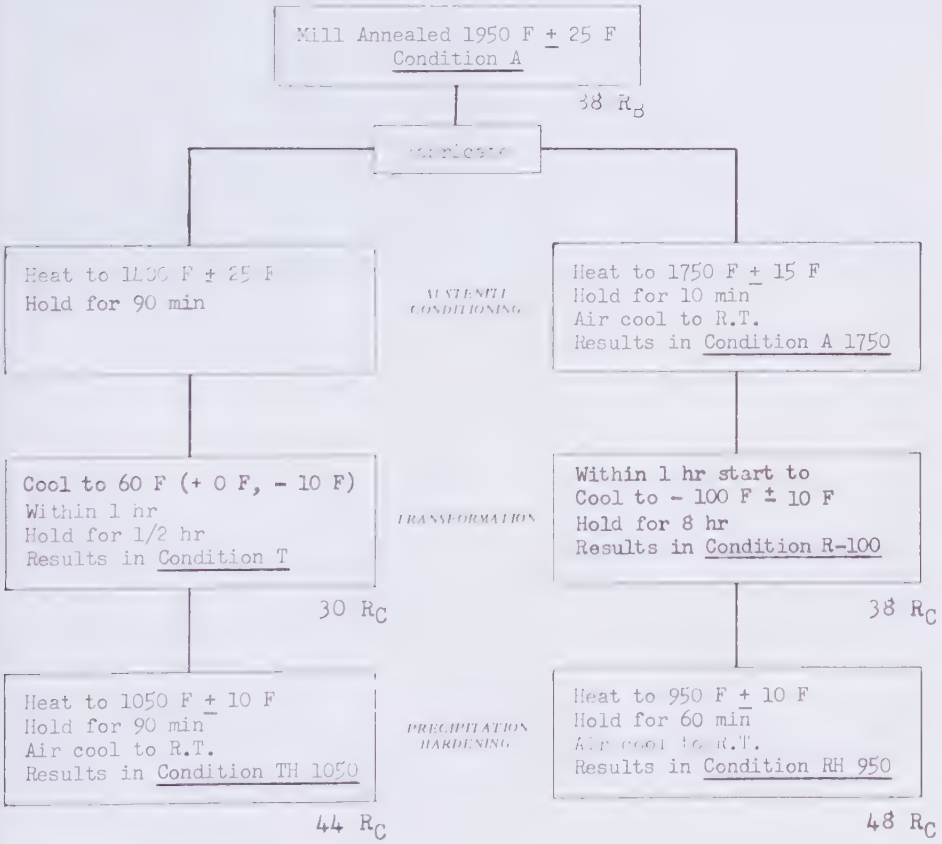
TABLE I.—SPECIFIED CHEMICAL COMPOSITION FOR 17-7 PH AND PH 15-7 Mo STAINLESS STEELS.

Element	17-7 PH	PH 15-7 Mo
Carbon, max, per cent	0.09	0.09
Manganese, max, per cent	1.00	1.00
Phosphorus, max, per cent	0.04	0.04
Sulfur, max, per cent	0.04	0.04
Silicon, max, per cent	1.00	1.00
Chromium, per cent	16.00 to 18.00	14.00 to 16.00
Nickel, per cent	6.50 to 7.75	6.50 to 7.75
Aluminum, per cent	0.75 to 1.50	0.75 to 1.50
Molybdenum, per cent		2.00 to 3.00

Specimens treated to conditions T, TH 1050, R-100, and RH 950 are etched by immersing 1 to 2 min in a solution consisting of 5 ml hydrochloric acid, 1 g picric acid, and 100 ml methyl alcohol (Vilella's reagent). It is sometimes necessary to immerse electropolished specimens in a dilute 10 per cent hydrochloric acid - water solution to activate the surface and obtain uniform etching.

When specimens are heat treated to condition T and age hardened to condition TH 1050, the matrix transforms to

TABLE II.—HEAT TREATMENTS FOR 17-7 PH AND PH 15-7 Mo STAINLESS STEELS.


Mill Annealed 1950 F ± 25 F
Condition A
38 R_B
Heat to 1400 F ± 25 F
Hold for 90 min
AUSTENITE CONDITIONING
Heat to 1750 F ± 15 F
Hold for 10 min
Air cool to R.T.
Results in Condition A 1750
Cool to 60 F (+ 0 F, - 10 F)
Within 1 hr
Hold for 1/2 hr
Results in Condition T
TRANSFORMATION
Within 1 hr start to
Cool to - 100 F ± 10 F
Hold for 8 hr
Results in Condition R-100
30 R_C
38 R_C
Heat to 1050 F ± 10 F
Hold for 90 min
Air cool to R.T.
Results in Condition TH 1050
PRECIPITATION HARDENING
Heat to 950 F ± 10 F
Hold for 60 min
Air cool to R.T.
Results in Condition RH 950
44 R_C
48 R_C

a structure similar in appearance to tempered martensite (Fig. 2). The ferritic stringers are still present but are almost masked out by the general transformation of the matrix. Differences between conditions T and TH 1050 are not found using optical microscopy and this etchant.

4) and precipitation hardens. No evidence of an age hardening precipitate has been detected using the optical microscope.

ELECTRON MICROSCOPY

The nitric-acetic acid electrolytic etch and the hydrochloric-picric acid

FIG. 1.—Stringers of Ferrite in a Matrix of Austenite in PH 15-7 Mo Stainless Steel, Condition A (×1000).

Etch: Nitric-acetic acid, followed by oxalic acid; electrolytic.

FIG. 2.—Martensite Plus Ferrite Stringers in PH 15-7 Mo Stainless Steel, Condition TH 1050 (×1000).

Etch: Hydrochloric-picric acid (Vilella's reagent).

X-ray diffraction study of these steels in the hardened conditions indicates 3 to 8 per cent austenite, in addition to the martensite and ferrite, that is not discernible by either optical or electron microscopy.

In material cold treated to −100 F (condition R-100) the matrix is transformed to untempered martensite (Fig. 3). Heat treating at 950 F (condition RH 950) tempers the martensite (Fig.

reagent were also used on specimens for electron microscopy. Preshadowed positive carbon replicas were made by placing cellulose acetate tape on the surface of the etched micro specimen and wetting with a few drops of acetone. The tape was stripped from the specimen, taped to a glass slide (impression up), and placed in a vacuum deposition unit. Platinum was vapor deposited on the tape at an angle of 45 deg, then car-

bon was vapor deposited on the tape normal (90 deg) to the surface. The cellulose tape was dissolved away from the metal-carbon film by the Jaffe method.

Figure 5(*a*) is an electron micrograph of annealed (condition A) precipitation hardening stainless steel etched with the hydrochloric-picric acid reagent. In Fig. 5(*b*) the etchant was nitric-acetic acid, electrolytic. In the annealed condition these etchants attacked the specimens similarly; however, the nitric-acetic acid etch delineated the ferrite and austenite phases more sharply.

In condition T the structure of the precipitation hardening stainless steel consists of small globular carbides precipitated at the martensite-ferrite interfaces (Fig. 6(*a*)). In condition TH 1050 (Fig. 6(*b*)) a similar structure is observed; however, the martensitic matrix is more heavily attacked.

The nitric-acetic acid etch attacks the precipitation hardened stainless steels (conditions T and TH 1050) more severely than the hydrochloric-picric acid reagent (Figs. 7(*a*) and (*b*)). The carbide particles have been removed by this attack. However, there is a marked difference in the appearance of the martensite matrix of the TH 1050 material. A veined substructure is observed, while none is present in condition T material.

In conditions R-100 and RH 950 the structures are similar to conditions T and TH 1050 except the carbides are

FIG. 3.—PH 15-7 Mo Stainless Steel, Condition R-100 (×1000).

Matrix structure consists of untempered martensite. Etch: Hydrochloric-picric acid (Vilella's reagent).

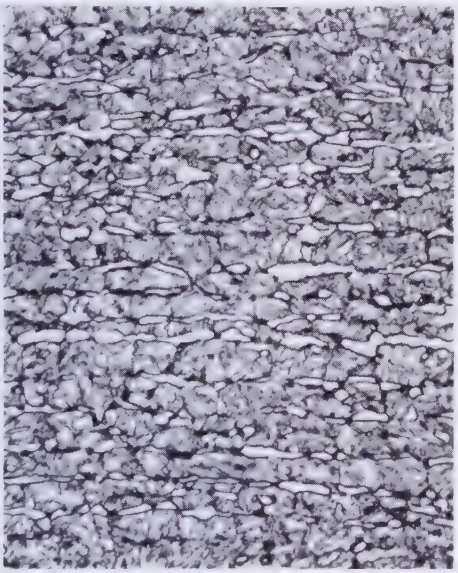
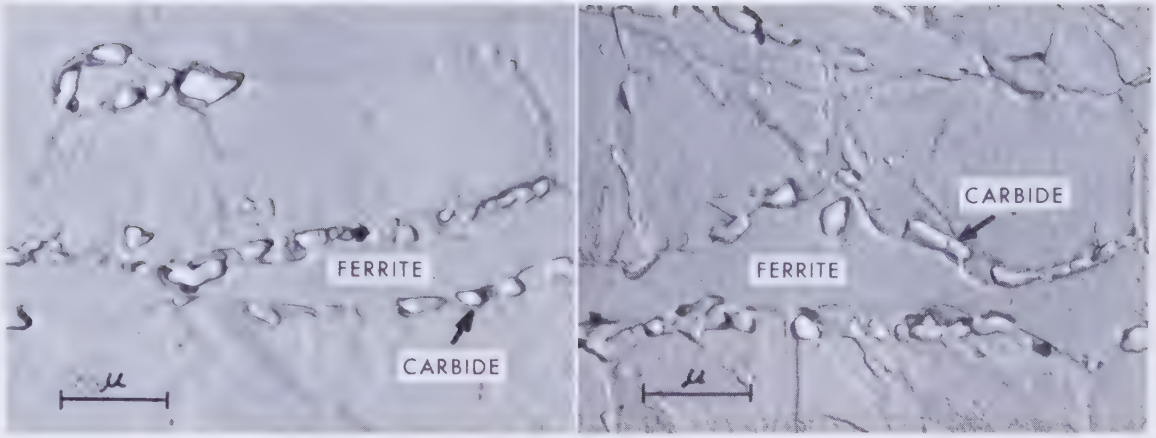


FIG. 4. PH 15-7 Mo Stainless Steel, Condition RH 950 (×1000).

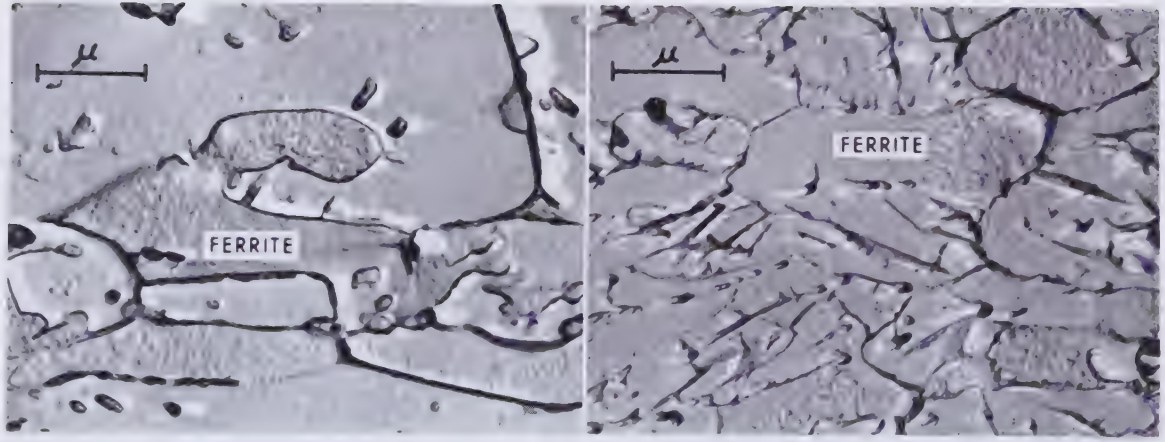
Matrix structure consists of tempered martensite. Etch: Hydrochloric-picric acid (Vilella's reagent).

FIG. 5.—(a) Hydrochloric-acid (Wahl's reagent). (b) Etch, Nital—acetic acid, followed by oxalic acid electrolytic. (c) 18-7 Mo Stainless Steel, Tentative A (Annealed) (X1800, reduced approximately one-fourth in reproduction)



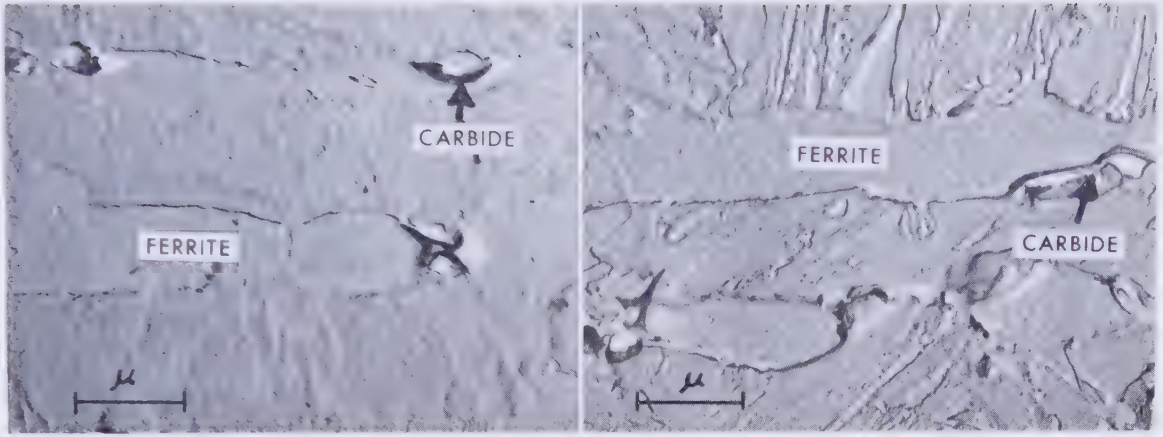
(*a*) Condition T. (*b*) Condition TH 1050.

FIG. 6.—PH 15-7 Mo Stainless Steel; Etch: Hydrochloric-Picric Acid (Vilella's reagent) (×18,000, reduced approximately one fourth in reproduction



(*a*) Condition T. (*b*) Condition TH 1050.

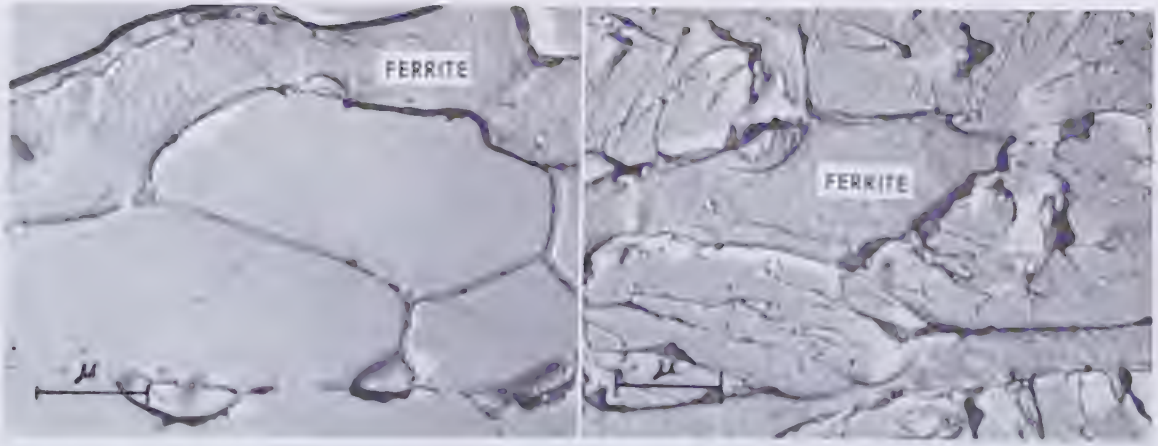
FIG. 7—PH 15-7 Mo Stainless Steel; Etch: Nitric-Acetic Acid, Followed by Oxalic Acid; Electrolytic (×18,000, reduced approximately one fourth in reproduction).



(*a*) Condition R-100. (*b*) Condition RH 950.

FIG. 8.—PH 15-7 Mo Stainless Steel; Etch: Hydrochloric-Picric Acid (Vilella's Reagent) (×18,000, reduced approximately one fourth in reproduction).

The above electron micrographs are similar to those in Fig. 6(*a*) and (*b*) except that the carbides are fewer.



(*a*) Condition R-100. (*b*) Condition RH 950.

FIG. 9—PH 15-7 Mo Stainless Steel; Etch: Nitric Acetic Acid, Followed by Oxalic Acid Electrolytic (X18,000 reduced approximately one fourth in reproduction).

The structures with this etchant are similar to those in Fig. 7(*a*) and (*b*) (conditions T and TH 1050).

fewer (Figs. 8(*a*) and (*b*)). These carbides are precipitated during austenite conditioning at 1750 F. The 1400 F austenite conditioning treatment (condition T) is near the temperature of maximum carbide precipitation as shown by the large number of carbides present in conditions T and TH 1050. These carbides form in greater quantity at the ferrite-austenite interfaces and in lesser amount in the austenite grain boundaries. This behavior has been substantiated by examining precipitation hardening steels of varying carbon content.

When specimens of steels in conditions R-100 and RH 950 are etched with the nitric-acetic acid reagent (Figs. 9(*a*) and (*b*)), the structures are similar to conditions T and TH 1050, respectively (Figs. 7(*a*) and (*b*)).

The age hardening treatment increased the hardness by 14 points Rockwell C between conditions T and TH 1050 and by 10 points Rockwell C between conditions R-100 and RH 950.

The precipitate causing age hardening in the precipitation hardening stainless steels has not been positively identified. It has been reported that nickel-chromium alloys containing aluminum are responsive to age hardening as the result of the precipitation of an intermetallic compound of the type Ni_3Al (8).[3] A compound of this type may cause the age hardening in the precipitation hardening stainless steels.

It is known that these precipitation hardening steels must first undergo transformation prior to age hardening. The process of transformation produces lattice dislocations. These dislocations serve as minute regions at which precipitation may occur. It is evident that the precipitate particles, if present, are very small, for the electron micrographs indicate only substructure veining (Figs. 6(*b*), 7(*b*), 8(*b*), and 9(*b*)) and do not show precipitated particles.

Acknowledgments:

The authors wish to thank Messrs. M. E. Carruthers, R. H. Heyer, M. W. Marshall, and D. C. Perry for their assistance in the preparation of this paper.

Appreciation is expressed to the management of Armco Steel Corp. for permission to publish these findings.

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SLIP LINES IN A PRECIPITATION-HARDENED NICKEL-BASE ALLOY*

By G. I. Madden,[1] D. L. Sponseller,[1] and W. C. Bigelow[1]

Many of the favorable high-temperature properties of the nickel-base heat-resistant alloys are well known to be due to an age-hardening process involving the precipitation of a fine dispersion of submicroscopic particles of the intermetallic γ' phase throughout the matrix of these alloys during aging and service at high temperatures. A number of papers have been published in recent years describing investigations of these alloys; however, it does not appear possible to understand completely the relationships between the microstructures and mechanical properties of these alloys because of a lack of information concerning the extent to which the γ' particles are coherent with the matrix at different stages in the aging process.

In studies of aluminum-copper and aluminum-magnesium alloys, Thomas and Nutting (**1**,**2**)[2] and Koda and Takeyama (**3**) have shown that indications of the state of coherency existing between precipitate particles and the matrix can be obtained from observations on the interaction of slip lines with precipitate particles in the surfaces of deformed specimens. In particular, it appears that at room temperature the slip lines pass through coherent or partially coherent particles, deforming them with the matrix, but bend around or stop at noncoherent particles. At liquid nitrogen temperature, however, the slip lines also passed through noncoherent particles. This paper describes some preliminary results obtained in attempting to use this technique to determine the state of coherency of the γ' precipitate particles in the nickel-base alloys.

Materials and Methods

An experimental alloy containing 79.2 per cent nickel, 16.3 per cent chromium, 2.61 per cent aluminum, 1.92 per cent titanium, and traces of boron and carbon was chosen for this investigation to avoid complications due to the formation of complex carbides and other phases such as occur in common commercial alloys of this type. A 3500-g ingot of this alloy was air-melted in a small induction furnace from refined metals of high purity. The ingot was homogenized for 6 hr at 2190 F (1200 C) and reduced 80 per cent by hot rolling at 2150 F (1175 C). Flat tension specimens and specimens for metallographic examinations and hardness measurements were cut from the rolled bar stock, solution treated at 1830 F (1000 C), and heat treated as follows:

(*a*) Water quenched from the solution temperature; aged at 1600 F (870 C) for periods ranging from 1 to 250 hr; water quenched.

(*b*) Furnace-cooled from the solution temperature to 1515 F (825 C) and held at this temperature for 48 hr, then water quenched.

* Presented at a Technical Session June 26, 1961, during the Sixty-fourth Annual Meeting of the Society.

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[2] The boldface numbers in parentheses refer to the list of references appended to this paper.

After mechanical polishing through No. 600 emery paper, the specimens were electrolytically polished in a solution consisting of 9 parts by volume of glacial acetic acid to 1 part of concentrated perchloric acid, and electrolytically etched in a solution consisting of 47 parts by volume of concentrated sulfuric acid to 12 parts of concentrated phosphoric acid and 41 parts of concentrated nitric acid, using procedures described previously (4). The specimens were then deformed bly overaged, respectively, as indicated by the variation in hardness of the alloy with aging shown in Fig. 1. These specimens contained numerous spheroidal γ' particles which increased in size and decreased in number with increasing periods of aging as shown in Figs. 2(*a*) to (*c*). The specimen that was furnace-cooled contained large cuboidal γ' particles which ranged up to 5000 Å on a side, as shown in Fig. 3.

Many interesting arrangements of slip

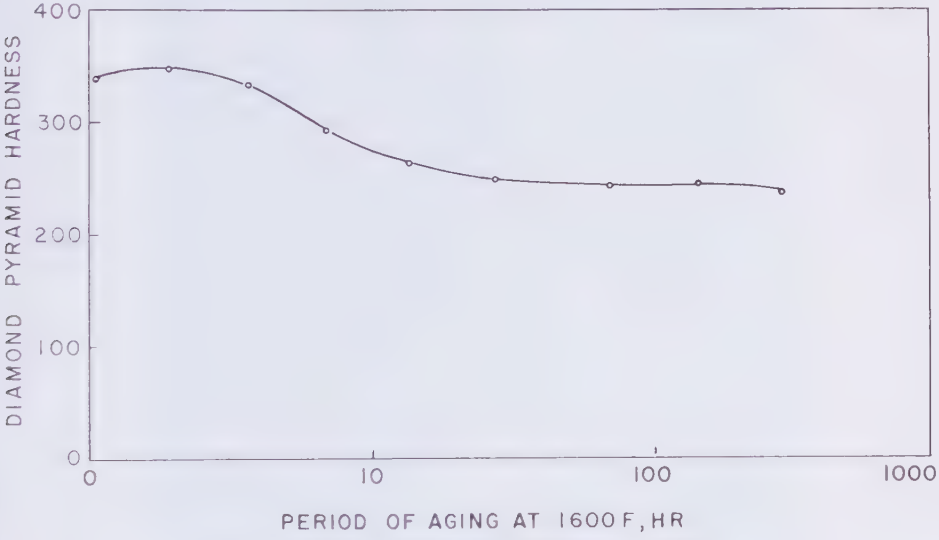

FIG. 1.—Variation in Hardness with Aging at 1600 F.

from 12 to 15 per cent in tension at room temperature and examined by electron microscopy using palladium-shadowed collodion replicas.

OBSERVATIONS AND DISCUSSION

Electron microscopic examinations were made of deformed tension specimens that had been aged 1, 30, and 250 hr at 1600 F (870 C) and of deformed tension specimens that had been furnace-cooled to, and aged at 1515 F (825 C). The specimens aged at 1600 F correspond approximately to conditions of optimum aging, slightly overaged, and considerable, similar to those reported in previous studies of slip structures by electron microscopy, were observed in the various specimens. In general, slip appeared to occur on individual slip planes which were relatively widely separated rather than on slip bands of closely spaced lamellae such as have been found in high-purity aluminum, copper, and silver (5). Figures 2(*a*) and (*b*) include portions of grains with slip occurring on two slip systems. Figures 2(*a*) to (*c*) show the termination of slip lines at grain boundaries. The amount of slip varied widely for different slip lines, and ranged from less

(*a*) Aged 1 hr.
(*b*) Aged 30 hr.
(*c*) Aged 250 hr.

FIG. 2.—Slip Lines in Specimens Aged at 1600 F (×8500).

than 100 Å to more than 1000 Å. This is to be expected for observations on randomly oriented grains in polycrystalline specimens since only the component of slip which is perpendicular to the surface of a particular grain would produce slip steps detectable by surface replicas.

One unique feature of the nickel-base alloys is the development of the cubic γ' particles under certain aging conditions. The γ' particles and the γ matrix phase both have cubic crystal lattices with nearly identical lattice parameters and the same crystallographic orientations (6). The cubic γ' particles can therefore often be used to deduce the crystallographic orientations of the individual crystal grains observed in the electron micrographs and to determine the orientations of the slip planes relative to the surface. For example, the observed trapezoidal and triangular sections of the γ' particles in Fig. 3 suggest that the surface of the specimen is approximately parallel to the (221) planes of the grain and would permit reasonably accurate calculations of the orientations of the two systems of slip lines relative to the surface and of the actual heights of individual slip steps.

The principal point of present interest, however, concerns the fact that in all of the specimens examined, the slip lines appeared to pass directly through the γ' particles. This is especially evident in Figs. 2(*b*) and (*c*) and 3. The arrows in Figs. 2(*b*) and (*c*) indicate particles that appear to have been extensively sheared by the slip. Based on the observations and conclusions of Nutting (1,2) and Koda (3) and their associates, this suggests that the γ' particles remain at least partially coherent with the matrix over the entire range of heat treatments used, from maximum hardness to considerable overaging, and for particles ranging from a few hundred Ångstroms to several thousand Ångstroms across. This is rather interesting, for in most precipitation hardening alloys loss of coherency is considered to coincide with overaging and to occur when the precipitate particles become a few hundred Ångstrom units across. Such prolonged coherency might be explained in terms of the facts that the γ' particles and matrix phase have similar crystallographic lattice dimensions and orientations, and would be consistent with the fact that the hardness of these alloys decreases only relatively slowly from the maximum value even with prolonged aging. Alternately, it is

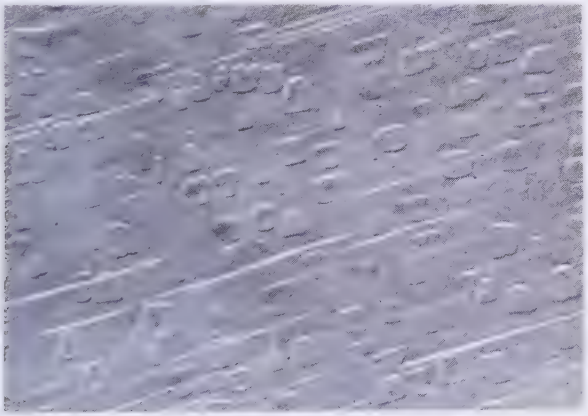

FIG. 3.—Slip Lines in Specimen Furnace Cooled and Aged 48 hr at 1515 F (×14,000).

possible that the γ' particles were actually noncoherent but that the slip lines did not bend around them because the necessary cross-slip mechanism was not thermally activated at room temperature. Nutting and associates observed similar shearing of noncoherent β particles in an Al-7Mg alloy when it was deformed at low temperatures. It is now planned to study the deformation of the nickel-base alloys at elevated temperatures and by thin film techniques to clarify this point.

Acknowledgment:

This work was assisted by a grant from the Horace H. Rackham School of Graduate Studies of the University of Michigan.

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A TECHNIQUE FOR REMOVING PLASTIC BACKING FILMS IN THE PREPARATION OF ELECTRON MICROSCOPE SPECIMENS*

By T. F. Beals[1] and W. C. Bigelow[2]

A relatively simple procedure has been developed which eliminates many of the difficulties frequently encountered in dissolving the thick layers of soluble plastics used as primary replicas in two-stage replica processes and as reinforcing or "backing" layers in the preparation of thin support membranes and direct replicas. The apparatus used in this procedure is a standard Soxhlet extractor which is equipped with a Z-shaped specimen carrier made of fine wire screen. The specimen carrier fits inside the extractor tube where it is held at a level slightly higher than the siphon tube by a wire or glass stand. The general features of this apparatus are illustrated in Fig. 1.

In using this apparatus, small pieces of the replicas or support membranes which are coated with the plastic backing layer are placed on electron microscope specimen grids which are then placed on the Z-shaped specimen carrier as shown in Figs. 1(*b*) and (*c*). An appropriate solvent for the backing layer is placed in the boiling flask of the extractor and heated until the apparatus is warmed by the vapor. When drops of the solvent begin to run from the condenser, the condenser is raised and the specimen carrier, bearing the grids and specimens, is inserted into the extractor tube. The condenser is then replaced and oriented so that the drops of solvent fall onto the top of the specimen carrier where they spread out and flow downward among the wires of the screen. As the solvent passes beneath the specimen grids, surface tension draws it up into contact with the specimen films where it dissolves the plastic backing layer as in the familiar Jaffe method.[3] The heating of the boiling flask is adjusted so that the solvent condenses and flows at a moderate rate over the specimen carrier, and the apparatus is then allowed to operate until solution of the backing layer is complete. The time required for this must be determined by experiment and may range from a few minutes to as much as one hour, depending on various factors such as the nature and thickness of the backing layer, the solvent used, and the rate of solvent flow. At the end of the period of washing, the specimen carrier is lifted from the extractor tube, whereupon the solvent quickly evaporates leaving the specimens clean, intact, and ready for examination.

This procedure offers several advan-

* Presented at a Technical Session during the Sixty-third Annual Meeting of the Society, June, 1960.

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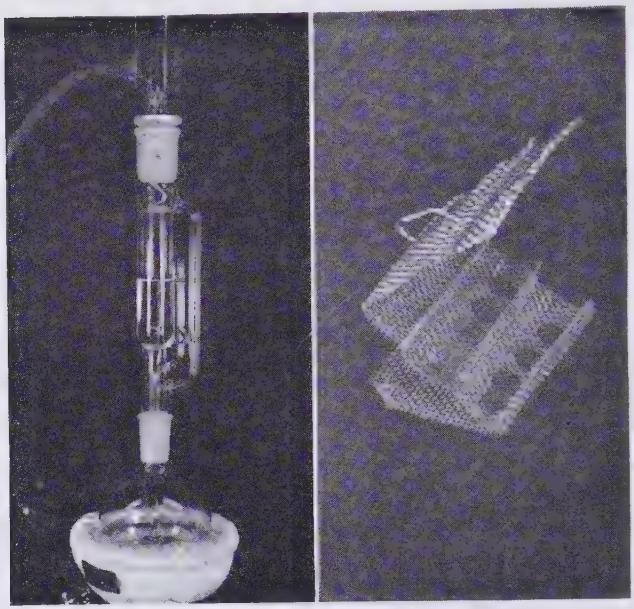
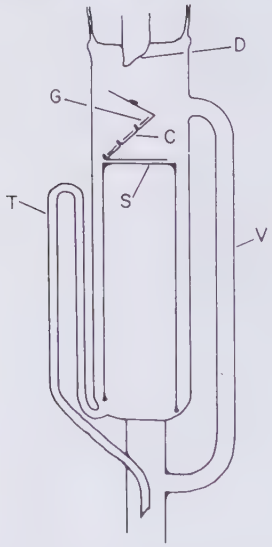
[2] Associate Professor, Department of Chemical and Metallurgical Engineering, University of Michigan, Ann Arbor, Mich.

[3] E. F. Fullam, "Replica Washing Methods," Symposium on Techniques for Electron Metallography, *ASTM STP No. 155*, Am. Soc. Testing Mats., p. 101 (1953).



(*a*) Assembled apparatus. (*b*) Specimen carrier.



(*c*) Diagram of extractor tube showing location and arrangement of the specimen carrier, *C*, the specimen grids, *G*, the carrier stand, *S*, the condenser tip, *D*, the siphon tube, *T*, and the vapor tube, *V*.

FIG. 1.—Soxhlet Extractor and Specimen Carrier for Dissolving Plastic Backing Films.

tages which make it especially convenient to use for many purposes. The apparatus is simple, inexpensive, and easy to obtain. A number of specimens can be processed at once with a minimum of handling and manipulation, and the operation is essentially automatic and requires no attention once the heat-

ing current has been properly established. With a proper rate of flow of solvent over the specimen carrier, the action is gentle enough so that even very thin carbon films are not damaged when plastic backing films are removed from them. The dissolving action is relatively efficient, and there is little danger of introducing contamination since the solvent in contact with the specimens is continuously renewed with the freshly distilled solvent that flows downward over the specimen carrier. It also appears that tearing of the specimen films due to swelling of backing layers is reduced in this apparatus, perhaps because the solvent vapors help to minimize surface tension and condense on the specimens, covering them uniformly with solvent as soon as they are inserted into the apparatus.

For best results it has been found desirable to construct the specimen carrier of platinum screen which can be easily and thoroughly cleaned by flaming, and which does not react with the various solvents to produce reaction products that may contaminate the specimens. The screen must also be sufficiently fine (at least 80 to 100 holes per inch) so that the drops of solvent falling from the condenser do not pass through it. Often it is helpful to reinforce the screen with a framework of heavier platinum wire to give the carrier greater rigidity and to make it easier to handle. It is also desirable to use an easily variable heating source such as an electric heating mantle powered by a variable transformer in order to obtain adequate control of the rate at which solvent condenses and flows down the specimen carrier, since too rapid a flow rate may cause the specimen films to break. Violent "bumping" of the solvent in the boiling flask also tends to break up the specimen films, and may be avoided by adding a few boiling stones

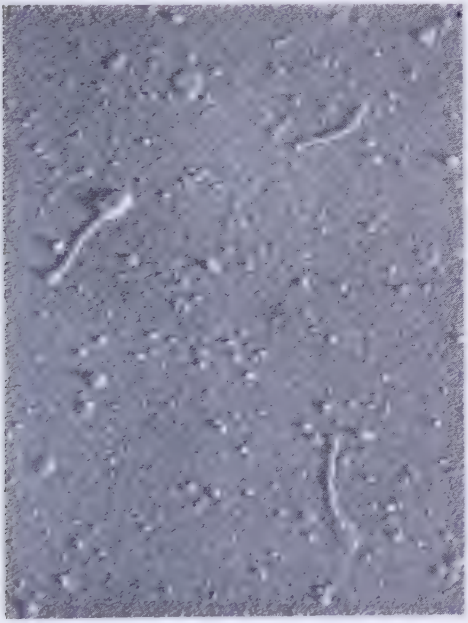


FIG. 2.—Staphylococcus Bacteriophage on Thin Carbon Support Film (×80,000).

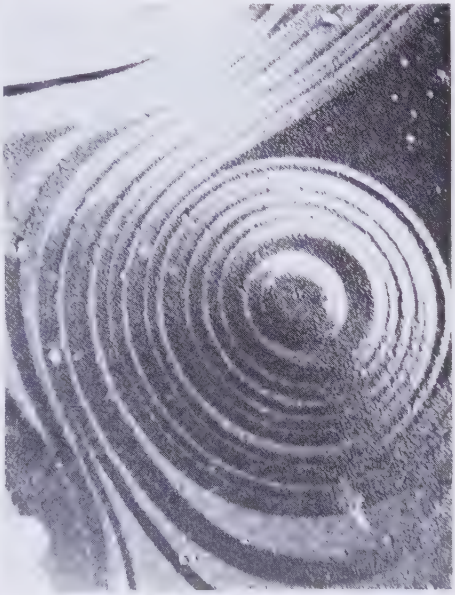


FIG. 3. Vapor Growth Structures on Internal Surfaces of Pores of a Sintered Ferrite Specimen (×30,000).

to the flask. For obvious reasons grease should not be used on the ground glass joints of the extractor apparatus.

This procedure has been used with considerable success for routine preparation of carbon replicas and support films for a variety of purposes. Four examples are shown in Figs. 2 to 5. Figure 2 is an electron micrograph of bacteriophage on a very thin carbon film which was prepared by evaporating carbon onto a Formvar film, and then dissolving the Formvar with chloroform in the apparatus described above. Figure 3 shows vapor growth structures observed within the pores of a sintered ferrite specimen by a two-stage replica process using heavy cellulose acetate tape for the primary replica and evaporated carbon for the secondary replica.[4] The cellulose acetate tape was dissolved from the carbon replica with acetone. Figure 4 is an electron micrograph of a ragweed pollen grain which was replicated by sprinkling pollen grains onto the surface of a thick collodion film which had been softened by exposure to amyl acetate vapors, allowing the surface to harden and brushing the pollen grains from it. A thin layer of carbon was then deposited over the surface and the collodion was dissolved away in the extractor, using amyl acetate as the solvent. Figure 5 shows TiN particles separated from a type 321 steel by the extraction replica technique.[5] The carbon replica film was supported during the extraction process by collodion which was subsequently dissolved with amyl acetate.

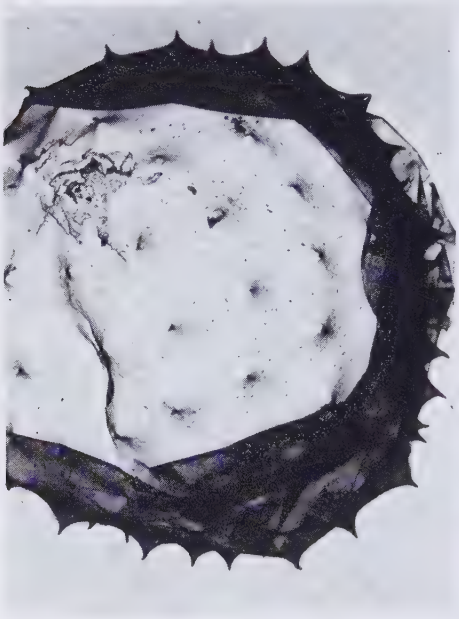


FIG. 4.—Carbon Replica of the Pollen Grain of Common Ragweed, *Ambrosia sp.* (×3600).

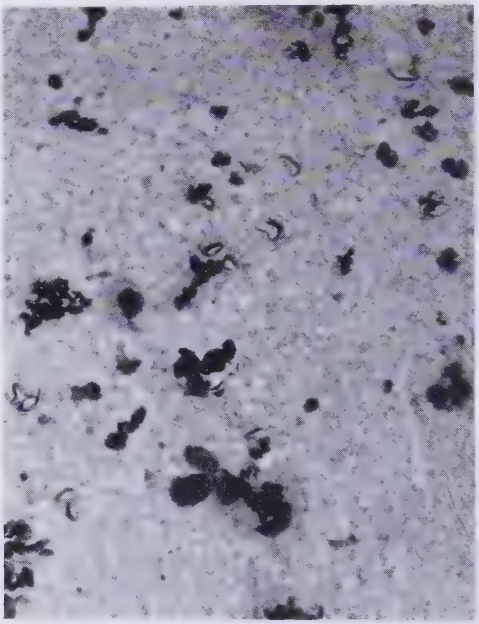


FIG. 5.—TiN Particles from Type 321 Steel on Carbon Extraction Replica (×14,500).

[4] J. Drobek, W. C. Bigelow, and R. G. Wells, "Electron Microscopic Studies of Growth Structures in Hexagonal Ferrites," *Journal*, Am. Ceramic Soc., Vol. 44, p. 262 (1961).

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Although these examples all involve the separation of various types of plastic backing materials from carbon specimen films, the solution procedure is equally useful for separation of other combinations of replica materials, provided a sufficiently selective solvent is used. By replacing the specimen carrier and the stand with a wire basket or similar device, the Soxhlet extractor can also be used for a variety of other purposes in the electron microscopy laboratory such as degreasing surfaces of specimens for examination by electron diffraction or microscopy, cleaning small instruments, and dissolving plastic replica films from recoverable specimen screens.

NITRIDE MORPHOLOGY IN 12 PER CENT CHROMIUM STEELS*

By B. R. Banerjee,[1] J. M. Capenos,[1] and J. J. Hauser[1]

Although the detailed morphology of chromium carbides has been extensively examined in stainless steels, the morphology of the $(FeCr)_2X$ nitride had not yet been characterized.

During the past decade the morphology of alloy-carbide precipitates in chromium steels was studied by light and electron metallography combined with X-ray and electron diffraction for identifying the carbide crystal structures. Mahla and Nielsen (1),[2] in an extensive electron microscope study of chromium carbides in type 304 stainless steel, found the $Cr_{23}C_6$ carbide to have a metastable dendritic morphology under certain precipitation conditions. Further details of the morphology of chromium-carbide precipitates in chromium steels have been revealed (2–8); Cr_7C_3 was found to have an acicular (7) and a dendritic (8) morphology.

Nitrides of the CrN and Cr_2N types were structurally characterized in considerable detail (9–16). The hexagonal nitride $(FeCr)_2N$ was reported in nitrided iron-chromium alloys (16) and was recently analyzed by X-ray fluorescence (17). A hexagonal Hägg-type double nitride of $CrMoN_2$ was found to have a needle-like morphology in a 16 per cent chromium, 25 per cent nickel, and 6 per cent molybdenum alloy (14); morphology of the Cr_2N nitride was concluded to be acicular (8) by examining chemically isolated precipitates and extraction replicas from 13.4 per cent chromium steels, where both carbides and nitrides were simultaneously present. Recently the morphology of iron-nitride precipitate was determined (9). However, the morphology of the chromium nitride (Cr_2N), or the Fe-Cr double nitride (designated M_2X (15) because of its variable carbon content) has not been clearly established.

In type 410 stainless steel oil quenched from 1800 F and tempered at 1100 to 1300 F, three carbides (M_3C, M_7C_3 and $M_{23}C_6$) are found (18). In addition, X-ray diffraction of the electrolytically extracted residue suggests the presence of chromium nitrides (see Table I). Also, chemical analysis of the extracted residue shows that, while upon tempering at 800 F the residue contains only 1.26 per cent nitrogen, the nitrogen content of the residue becomes 2.35 per cent upon tempering at 1300 F (18). At 800 F tempering carbides only are present, whereas at 1300 F nitrides are additionally present. The average nitrogen content of the type 410 stainless steel was 0.03 per cent. Figure 1, showing an extraction replica micrograph from type 410 stainless steel, does not permit a clear distinction between the carbides and nitrides or a

* Presented at a Technical Session June 26, 1961, during the Sixty-fourth Annual Meeting of the Society.

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[2] The boldface numbers in parentheses refer to the list of references appended to this paper.

TABLE I.—INTERPLANAR SPACINGS OF PRECIPITATES WITHIN MARTENSITE OF TYPE 410 STAINLESS STEEL TEMPERED 2 HR AT 1100 F.

Observed		M_7C_3[a]		M_2X		MX	
d, Å	*I*	*d*	*I*	*d*	*I*	*d*	*I*
2.43	MS	...	...	2.39	S	2.394	S
2.33							
2.27	W	2.28	50				
2.14	S	2.11	50	2.111	VS		
2.045	S	2.03	100			2.068	VS
1.89	M	1.89	10				
1.82		1.84	20				
1.79		1.80	40				
1.64	W			1.632	M		
1.50							
1.45		1.43	20			1.463	S
1.395	MS			1.382	W		
1.353		1.34	20				
1.300		1.32	10				
1.252		1.25	10	1.265	MW	1.249	M
1.237		1.199	40	1.196	MS	1.197	W
1.170	MS	1.175	40	1.178	MS		

[a] $M_{23}C_6$ was present in boundaries.

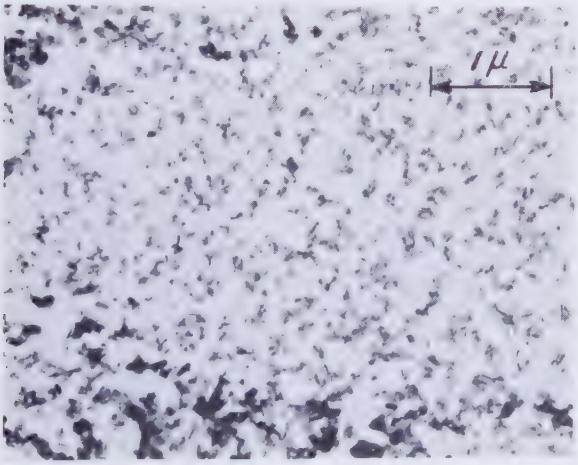


FIG. 1—Type 410 Stainless Steel Tempered 2 hr at 1100 F

description of their characteristic morphology.

EXPERIMENTAL PROCEDURE

To characterize the morphology of nitride precipitates from steels containing 12 per cent chromium, four experimental heats, having nitrogen contents of 0.002 and 0.09 per cent and carbon contents of 0.08 and 0.20 per cent respectively, were austenitized at 1800 F for 1 hr and oil quenched; they were subsequently tempered for 2 hr at 1100 and 1300 F respectively (Table II).

In studying morphology of carbides in chromium steels, the metal matrix is generally dissolved (1–7) in an acid or halogen-alcohol type of solution to

disperse the nitrides in the liquid, and the separated solid particles are transferred onto a film support. In this nitride morphology study of steels containing varying nitrogen and carbon, an extraction-replica technique yielded consistently better results in revealing not only the morphology but also the precise distribution of precipitate as it existed in the metal matrix.

This extraction-replica technique consisted of lightly etching the polished metal surface in Vilella's reagent, followed by evaporating carbon onto the surface and backing up the carbon film with Parlodion, deposited from a solution of Parlodion in *n*-butyl acetate. The precipitates were then removed from the steel matrix by etching through the replica with Vilella's reagent until the replica floated free onto the liquid surface. The replica pieces were rinsed in methyl alcohol, lifted directly on a grid, and examined in the electron microscope. A Phillips EM-100B instrument was used to examine the morphology and to obtain electron diffraction patterns.

TABLE II.—CARBON AND NITROGEN CONTENTS OF 12 PER CENT CHROMIUM STEELS.

Steel	Content, per cent	
	Carbon	Nitrogen
Type 410	0.11 (0.15 max)	0.026
A	0.07	0.002
B	0.19	0.002
C	0.08	0.077
D	0.20	0.092

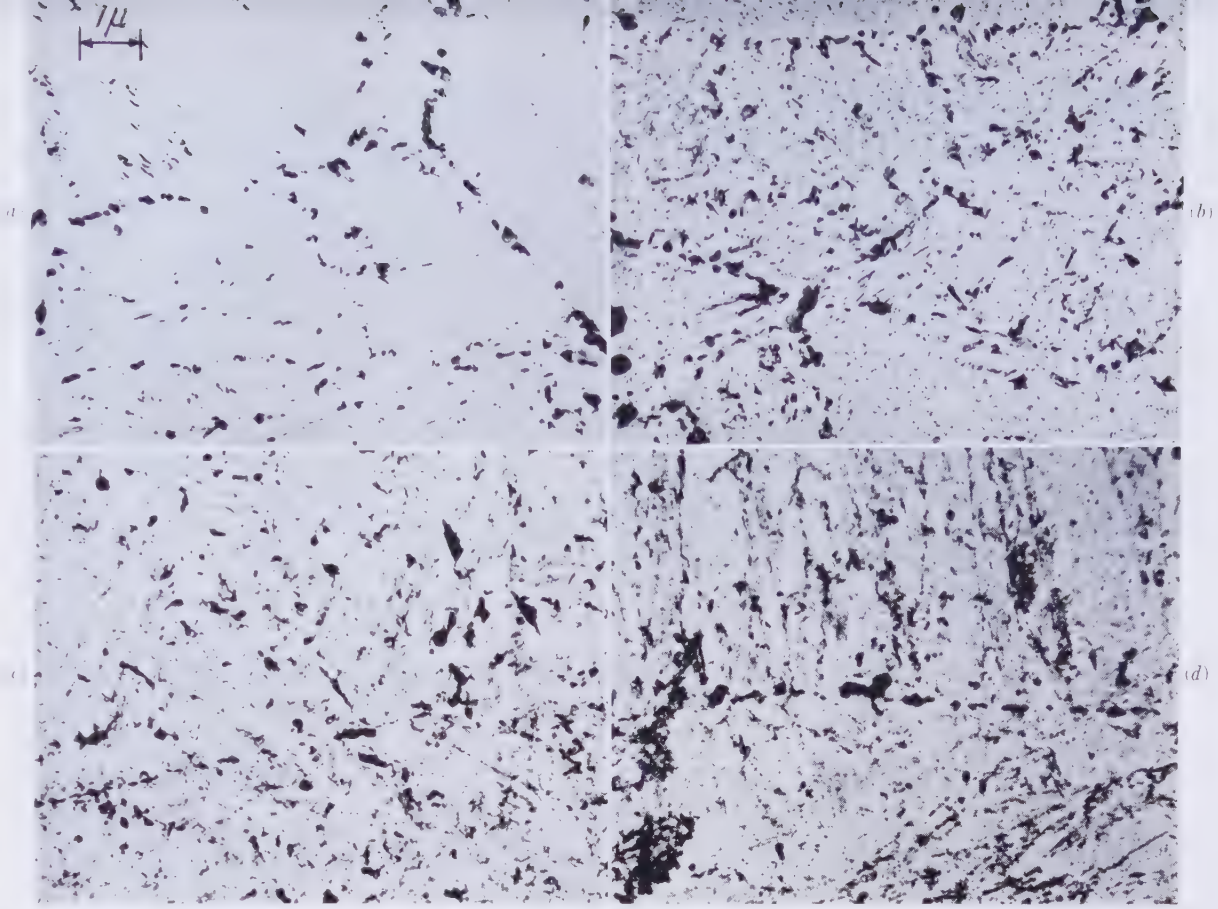
TEST RESULTS

Electron microscopy of carbon-extraction replicas prepared from specimens of the four 12 per cent chromium steels—containing low nitrogen low carbon, high nitrogen low carbon, low nitrogen high carbon, and high nitrogen high carbon respectively—revealed a dendritic morphology of the M_2X nitride. Electron and X-ray diffraction were used to identify the precipitates.

Figure 2 shows extraction replicas of specimens from the four heats, oil quenched from 1800 F and tempered 2 hr at 1100 F. Clearly the amount of precipitate increases with carbon, with nitrogen, and with total interstitial (carbon plus nitrogen) content; a finer precipitate forms upon increasing nitrogen than upon increasing the carbon content. In the high-nitrogen steels M_2X nitride was present, in addition to the $M_{23}C_6$ carbide which was present in all the steels. In the low-nitrogen high-carbon steel M_7C_3 was present in addition to $M_{23}C_6$.

Upon tempering at 1300 F, the precipitates coalesced to reveal their morphology and habit characteristics (Fig. 3). The rods and plates in the low-nitrogen high-carbon steel (steel B, Fig. 3(*b*) were $M_{23}C_6$. The M_2X nitride has a characteristic dendritic morphology, as seen in a few regions of the high-nitrogen low-carbon steel (steel C) in Fig. 3(*c*). Figure 4 shows one of these dendritic M_2X nitride particles at a higher magnification, clearly illustrating its characteristic morphology. The dark regions and bands within the dendrite are interference fringes caused by varying plate thickness. The irregular dendritic geometry is perhaps determined by the degree of registry of atom planes at the interface of the precipitate-habit plane, and the perfection of the matrix-atom plane on which the precipitate plate grows.

Electron diffraction patterns from the dendritic nitride exhibit pronounced arcing, suggesting preferred orientation of the dendrite branches; the absence of (002) reflection from the diffraction patterns suggests that the habit plane of the



(*a*) Steel A, low nitrogen, low carbon; $M_{23}C_6$.
(*b*) Steel B, low nitrogen, high carbon; $M_{23}C_6 + M_7C_3$.
(*c*) Steel C, high nitrogen, low carbon; $M_{23}C_6 + M_2X$.
(*d*) Steel D, high nitrogen, high carbon; $M_{23}C_6 + M_2X$.

FIG. 2.—Chromium Steels (12 per cent) Containing Variable Nitrogen and Carbon Tempered 2 hr at 1100 F.

(*a*) Steel A, low nitrogen, low carbon; $M_{23}C_6$.
(*b*) Steel B, low nitrogen, high carbon; $M_{23}C_6$.
(*c*) Steel C, high nitrogen, low carbon; $M_{23}C_6 + M_2X$.
(*d*) Steel D, high nitrogen, high carbon; $M_{23}C_6 + M_2X$.

dendritic plate is the basal plane of the hexagonal prism. The observed interplanar spacings of M_2X, from X-ray diffraction data shown in Table III, give

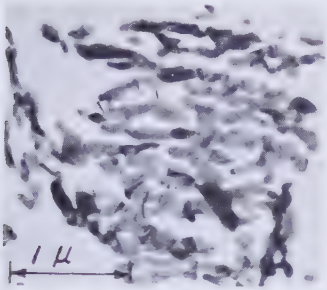


FIG. 4.—Dendritic Morphology of M_2X Nitride in Steel C Tempered 2 hr at 1300 F.

TABLE III.—OBSERVED INTERPLANAR SPACINGS OF M_2X NITRIDE FROM STEEL C.

HKL	*d*, Å	*I*
101	3.050	VW
110	2.414	M
002	2.225	MS
111	2.124	VS
112	1.638	M
300	1.394	MS
113	1.265	MS
203	1.211	W
302	1.182	S
221	1.165	S

lattice parameter values of $a_0 = 4.828$ Å and $c_0 = 4.457$ Å. The c to a ratio of 0.923 suggests a nitrogen-rich rather than a carbon-rich M_2X (**19**); this was confirmed by nitrogen analysis of extracted residues from steels A and C, tempered at 1300 F, which gave nitrogen contents of 0.22 and 3.72 per cent respectively. The M_2X nitride structure is consistent with a superlattice model, where the nitrogen atoms are ordered, occupying octahedral interstices in the hexagonal close-packed lattice, such that one half of the interstices are occupied and each nitrogen atom has an unoccupied hole above and below it in adjacent planes (**20,21**).

SUMMARY

A dendritic morphology of M_2X nitride was characterized for hardenable straight-chromium stainless steels by means of an extraction-replica electron microscope investigation of four steels containing 12 per cent chromium but variable nitrogen and carbon tempered at 1100 to 1300 F. The M_2X nitride has a hexagonal close packed lattice, having the following parameters: $a_0 = 4.828$ Å, $c_0 = 4.457$ Å, and c to a ratio = 0.923.

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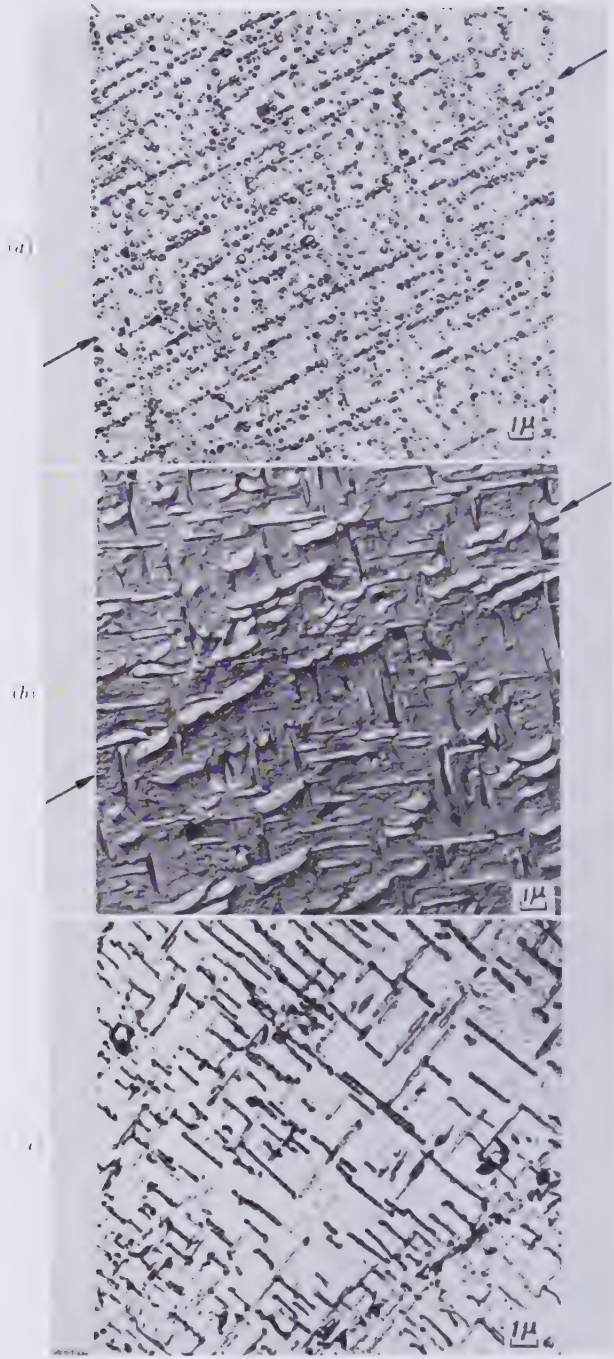


(*a*) After dissolution of a few microns of surface.
(*b*) Deeper region than (*a*).
(*c*) Still deeper region where no deformed superficial layer exists.

FIG. 1.—Electron Micrograph of Al-4Cu Specimen Solution Treated at 540 C for 2 hr, Water-Quenched, Ground in the Direction of the Arrows, and Aged at 260 C for 2 hr (×4000).

chanical finishing. It was solution treated at 540 C for 2 hr, water-quenched, and the surface ground again on 000 emery paper in one direction. It was then aged at 260 C for 2 hr, avoiding oxidation of the surface. The surface prepared in this way was dissolved away in small increments by electropolishing, as before. After each stage of dissolution, the surface was etched with 1*N* NaOH solution for 30 sec, and gold-shadowed cellulose acetate - carbon replicas were prepared for observation by electron microscopy.

After dissolution of a few microns of the surface metal, many small, granular, spheroidal particles about 0.3 μ in diameter were found along the scratch lines (Fig. 1(*a*)). These particles did not have

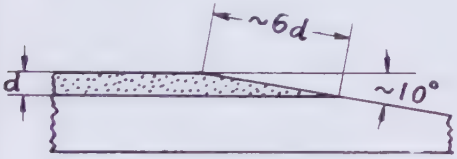


FIG. 2.—Oblique Section of Surface.
Thickness d enlarged to ~6 d with angle of cutting 10 deg.

the characteristic shape of the ordinary θ' phase precipitate particles which are platelets crossing perpendicular to each other. With further dissolution of the surface, these spheroidal particles disappeared and larger precipitate particles were observed along the direction of grinding (Fig. 1(*b*)). These were platelike in shape and resembled θ' particles except that they were several times thicker than the θ' platelets ordinarily observed. With still further dissolution of the surface, these precipitate particles were replaced by the ordinary θ' phase platelets described above (Fig. 1(*c*)).

Further information on the character of the precipitate at different depths was obtained by observations on a section cut at an angle of about 10 deg to the original surface, in the manner described by Jacquet,[2] so that the depth of the disturbed layer was effectively enlarged about 6 times as shown in Fig. 2. For this purpose, the surface was ground and a thick layer of aluminum was deposited onto it by evaporation to protect the surface layer to be observed from deformation during cutting. The specimen was then embedded in a phenolic resin and both were cut together by superfinishing. The obliquely cut surface was again dissolved electrolytically to eliminate the surface layer which would be deformed even by superfinishing. The section thus obtained permitted the change in the state of deformation of the crystals to be observed continuously from the top of the highly deformed surface layer to a depth where there was no deformation. Since the regions of interest were too large for a single electron micrograph, even under a low magnification, micrographs of many adjoining areas were mounted together to reproduce these larger areas.

One such interesting composite micrograph is shown in Fig. 3. The boundary of the surface, which is deeply etched because the aluminum protecting layer dissolved more rapidly than the Al-4Cu alloy in the NaOH etching solution, is indicated by arrows. The upper right-hand part of Fig. 3 seems to show grooves which resulted directly from the grinding. In the case of comparatively coarse grinding, such as is produced by the 000 emery paper on light alloys, some regions are subject to direct cutting while others are left without it,[3] as shown schematically in Fig. 4, although the latter are nonetheless influenced by the cutting which occurred near by. Figure 5 shows the oblique section under a low magnification observed by optical microscopy. The grooves were cut directly by abrasive edges, but from the submicroscopic point of view, the part of direct contact between one abrasive particle and the surface of the specimen is almost

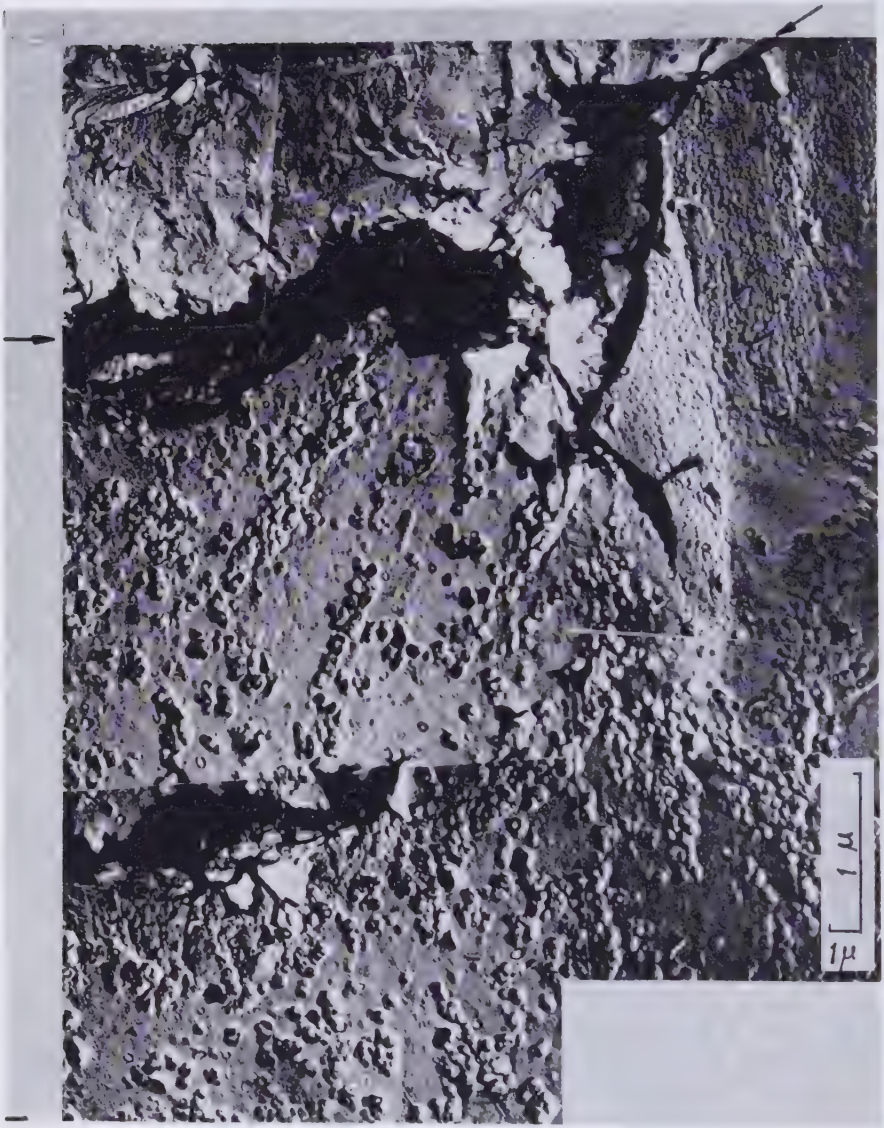


FIG. 3.—Electron Micrograph of Al-4Cu Specimen Surface Cut as in Fig. 2; Same Treatment as Fig. 1.

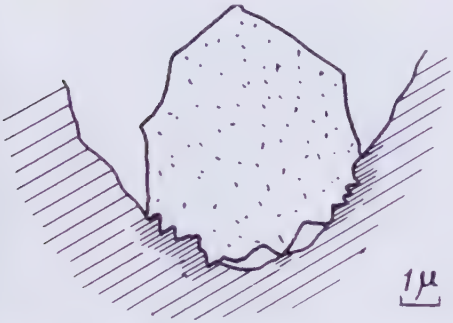


FIG. 4.—Schema of Microscopic Cutting with One Abrasive Particle.

but appeared at greater depths. Figure 6 is a micrograph of a slightly deeper region where two kinds of precipitate particles coexist. At depths of about 10 μ the spheroidal particles disappeared completely and only normal θ' platelets remained, as was the case in the observations normal to the surface.

The observations clearly show that the state of precipitation in surface regions which are disturbed mechanically by grinding is quite different from that in deeper regions where the crystal

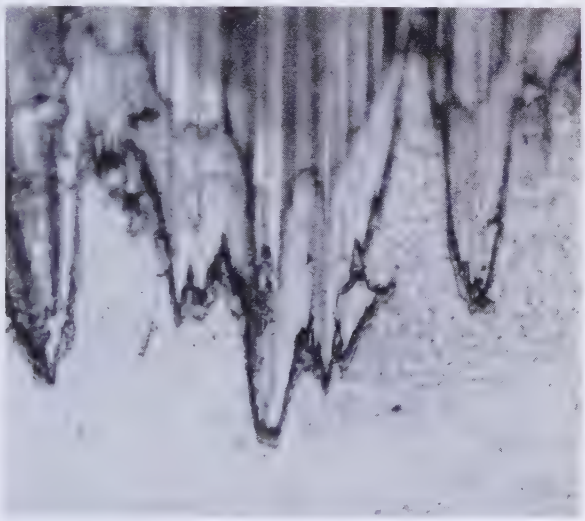


FIG. 5.—Photomicrograph by Light Microscope of Al-4Cu Specimen Surface Cut as in Fig. 2 (×500).

point contact of several abrasive protuberances which produce some minute scratch lines on the surface.

In most of Fig. 3, the precipitate particles appear to be spheroidal and to correspond to those shown in Fig. 1(*a*), above. These spheroidal particles extend to the depth of about 6 μ below the surface, with some local variations which probably result from variations in the conditions of grinding, such as pressure, speed, or size of abrasive particles. The ordinary θ' phase platelets do not seem to be present in the region of Fig. 3,

grains are not mechanically deformed. In addition, it appears that the grooves produced in surfaces by grinding influence precipitation in a manner somewhat similar to grain boundaries and slip lines. This is not surprising, for the grooves undoubtedly are high-energy structural regions, since it is well known that the grinding process causes marked local increases in temperature as well as mechanical deformation in the surface grains.

Some additional interesting observations on the influence of mechanical de-

formation on the θ' precipitate were made on a surface of the Al-4Cu alloy which was scratched with a knife blade. Figures 7(*a*) and (*b*) are electron micrographs obtained from replicas taken from the region of the scratches. The state of precipitation near the scratches is clearly different from that in the surrounding region which is not disturbed mechanically. The central region in Fig. 7(*a*) shows a cluster of precipitate particles near an indentation produced by the tip of the knife blade. Figure 7(*b*) shows spheroidal precipitate particles along the trace of a scratch, some of which are of the same order of size as those seen in Fig. 3.

Although scratching a surface with a knife blade is not the same as grinding it, there is some resemblance in that both processes involve a cutting action with a tool edge (in one case on a macroscopic scale and in the other case on a microscopic one, with the latter a much more complicated physical phenomenon). It is interesting that both processes appear to cause somewhat similar differences in the state of precipitation in the plastically deformed regions as compared to that in neighboring undeformed regions.

Because of the heat treatment used, it is believed that all of the spheroidal particles shown in Figs. 1(*a*), 3, 6, and others are the θ' phase.[4] The appearance of platelet precipitate particles of θ' phase is closely related to the fixed orientation between this phase and the matrix. In the region deformed plastically by mechanical finishing, this relation seems not to lead to the development of the characteristic crystals shaped like crossed platelets, in spite of the same heat treatment as in nondeformed regions. The former region would be under

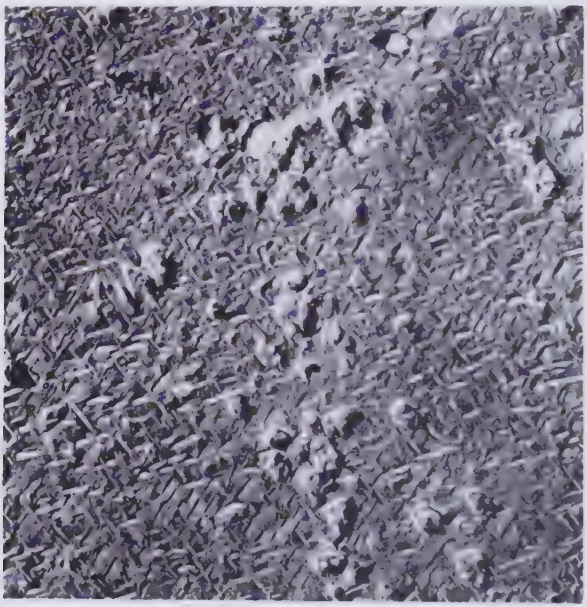
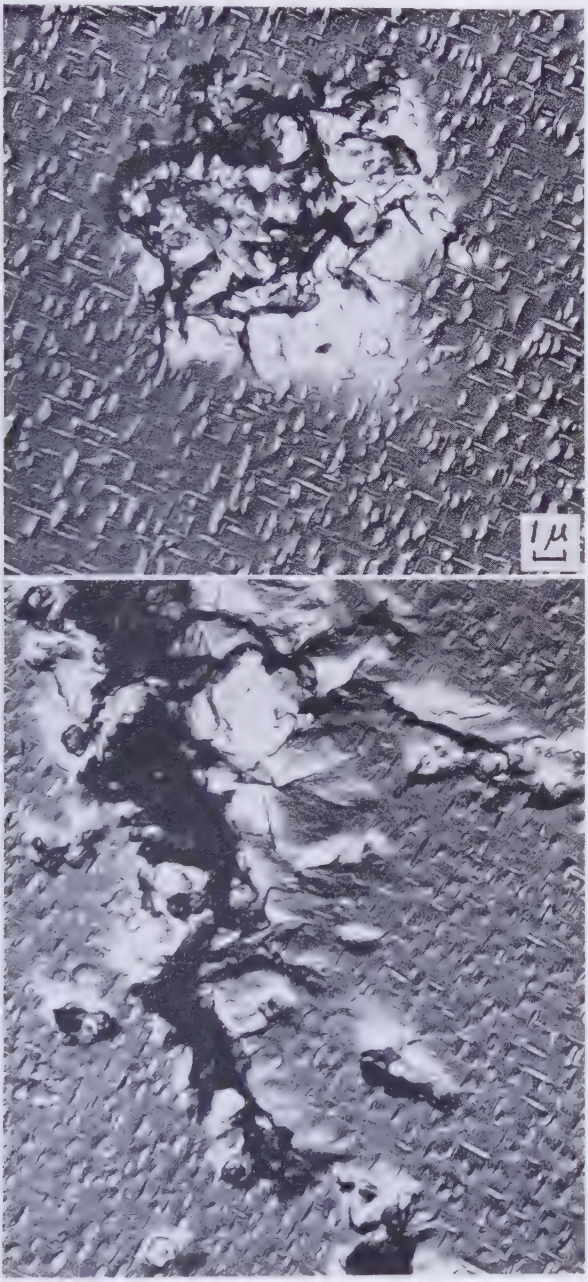


FIG. 6.—Same Specimen as Shown in Fig. 3, but a Much Deeper Region (×4000).

[4] The same kind of precipitate of θ' phase has been produced in thin metal films formed by electrolytically thinning mechanically rolled foils, when the thinned films were heated inside the electron microscope.



(*a*) Picked with tip of knife blade
(*b*) Scratched with knife blade

FIG. 7.—Electron Micrograph of Al-4Cu Specimen Solution Treated at 540 C for 2 hr, Water Quenched, Mechanically Deformed with Knife Blade, and Aged at 260 C for 2 hr (×4000).

heavy stress, which produces crystal imperfection including dislocations and perhaps prevents the normal development of the ordinary platelet θ' phase precipitate. The conditions in these deformed regions seem to be similar to those existing in grain boundaries and along slip lines insofar as their influence on the precipitation of the θ' phase is concerned. Electron microscopic studies of the kinetics of the θ' precipitation process are now planned to elucidate the relation between mechanical surface deformation and precipitation. Studies of the state of deformation due to surface finishing, utilizing the precipitation of a second phase from a supersaturated solid solution, are also planned for alloys other than Al-4Cu.

Acknowledgments:

The authors wish to offer their sincere thanks to Mr. Y. Watanabe of the Research Institute of Japan Light Metals Co. for his preparation of the specimens, to T. Asaeda and R. Nishimoto of Tokyo Institute of Technology for their help in making oblique sections by superfinishing of the specimens, and to W. C. Bigelow of The University of Michigan for assistance in preparation of the manuscript in English. This work was carried out with the aid of the Scientific Research Fund of Japanese Ministry of Education.

MULTIPLE REFLECTION PHENOMENA IN ELECTRON DIFFRACTION*

By H. J. Beattie, Jr.[1]

Occurrence of Forbidden Reflections

A diffraction phenomenon that is rare for X-rays but very common for 50- to 100-kv electrons is a principal source of difference between X-ray and electron diffraction intensities. Workers at our laboratory first became aware of this effect and its extent after examining electron diffraction patterns of cuprite (Cu_2O) in a Phillips EM 100A electron microscope at an accelerating potential of 100 kv. The powder pattern (Fig. 1) contains every possible reflection from a primitive cubic lattice. The strongest lines are those of a face-centered cubic lattice—that is, the Miller indices are all even or all odd. Lines having mixed indices with even sums are of intermediate intensity, while those having one odd and two even indices are the weakest set. There are only a few spots on each Debye ring of the latter set.

The cuprite structure consists in part of a face-centered cubic sublattice of copper atoms. The oxygen atoms are located in tetrahedral interstices of the copper lattice at $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ and $(\frac{3}{4}, \frac{3}{4}, \frac{3}{4})$, and thus form a body-centered cubic sublattice of the same unit cell dimension. The oxygen sublattice allows only reflections with indices having an even sum; they either combine with the even face-centered cubic reflections or belong to the set of lines observed as having intermediate intensity. The third set with one odd and two even indices cannot be reflected by either the copper or oxygen sublattice. A formal structure-factor calculation shows that these are systematic extinctions. The powder pattern, however, records all of these forbidden reflections.

A Laue pattern of cuprite (Fig. 2) shows all of the "forbidden" reflections in a [110] zone.

Theory

An explanation for the occurrence of forbidden reflections is found in two theoretical developments in the literature. They take entirely different approaches, one being kinematic and the other dynamic, but they result in specifying identical conditions for the occurrence of forbidden reflections.

Renninger's analysis (1),[2] which is described by Lipson and Cochran (2), considers the possibility that X-rays, after having been reflected by a particular set of planes $(h_1k_1l_1)$, may be reflected again by a second set of planes $(h_2k_2l_2)$ before leaving the crystal. For this double reflection to occur, rays that have been reflected by $(h_1k_1l_1)$ must be in proper orientation with respect to $(h_2k_2l_2)$ for Bragg reflection. Thus, the Ewald sphere in reciprocal space aligned on the direction of the incident beam must intersect the reciprocal lattice point $(h_1k_1l_1)$; then the Ewald sphere for the reflected ray

* Presented at a Technical Session June 26, 1961, during the Sixty-fourth Annual Meeting of the Society.

[1] Materials and Processes Laboratory, General Electric Co., Schenectady, N. Y.

[2] The boldface numbers in parentheses refer to the list of references appended to this paper.

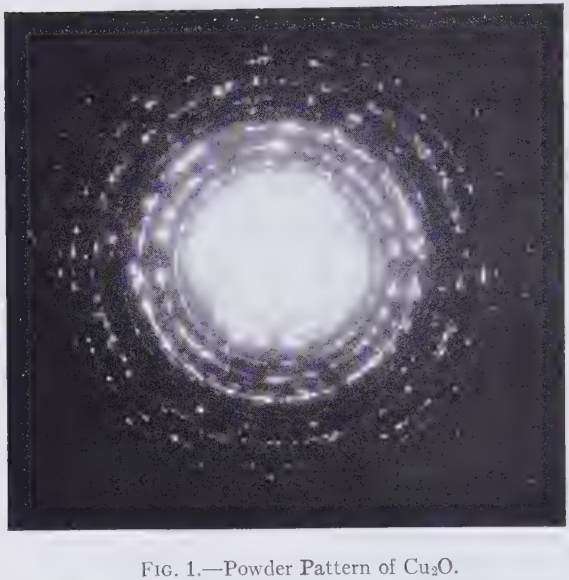


FIG. 1.—Powder Pattern of Cu_2O.

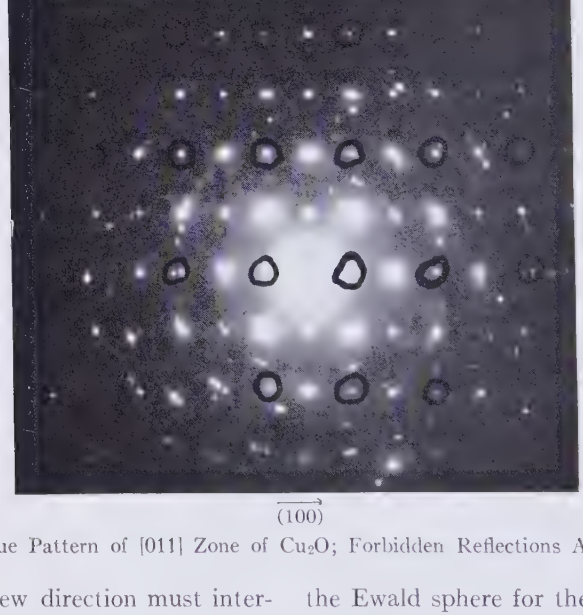


FIG. 2.—Laue Pattern of [011] Zone of Cu_2O; Forbidden Reflections Are Encircled.

oriented in a new direction must intersect the point $(h_2k_2l_2)$. It can be shown (1,2) that when this condition is met, the doubly reflected ray will appear to have been reflected from planes $(h_3k_3l_3)$, such that $h_3 = h_1 + h_2$, $k_3 = k_1 + k_2$, and $l_3 = l_1 + l_2$. Furthermore, these double Bragg reflections are possible whenever the Ewald sphere for the incident beam simultaneously intersects the points $(h_1k_1l_1)$ and $(h_3k_3l_3)$; that is, it must simultaneously intersect the initial and resultant apparent reflection points, but not necessarily the intermediate point $(h_2k_2l_2)$. Therefore, a forbidden reflection can occur whenever (1) the Ewald sphere

simultaneously intersects an allowed and a forbidden lattice point, and (2) the vector difference of these two points is an allowed reflection. Implicit in the latter stipulation is the requirement that *the forbidden reflection must be a vector sum of two allowed reflections.*

In 1949 Heidenreich (**3**) discussed the dynamic theory of electron diffraction, treating the electron beam in the crystal as a high-energy conduction electron in band theory. It was shown that an electron beam whose wave vector terminates on an edge or corner of a Brillouin zone of the crystal involves at least three reflections with indices having a vector-sum relationship. This leads to the possible appearance of forbidden reflections. A more detailed description of this aspect appeared in 1950 (**4**), where the problem was specifically addressed to the occurrence of the forbidden (222) reflection for the diamond structure. Here it is shown that a forbidden reflection occurs when the wave vector terminates on the intersection of the Brillouin-zone plane for the forbidden reflection, g, with a Brillouin-zone plane for an allowed reflection, s, and that the forbidden reflection is somehow generated by interaction with a third allowed reflection ($\lambda = g - s$). Now a wave vector terminating on the intersection of two Brillouin-zone faces is equivalent to an Ewald sphere intersecting two reciprocal lattice points, as these are two alternative constructions to define conditions for Bragg reflection; the Ewald sphere for diffraction locus built on the wave vector, while Brillouin zones are diffraction loci constructed on the reciprocal lattice points. Thus, if we identify Heidenreich's s, g, and λ with the indices $(h_1k_1l_1)$, $(h_3k_3l_3)$, and $(h_2k_2l_2)$ respectively, both analyses give the same geometric relationship between the wave vector and the reciprocal lattice.

Although Heidenreich prefers to use the terms "perturbation" and "coupling" to designate the interaction with the intermediate reflection λ, it would seem that the equivalence with Renninger's description leaves little doubt that the interaction is specifically multiple reflection. On investigating the result of a wave vector terminating on a Brillouin zone edge or corner, Heidenreich, perhaps at first unwittingly, specified the condition for multiple reflection; the powerful theory of wave mechanics correctly predicted the result without, however, giving much insight as to mechanism.

The wave vector of a 100-kv electron is one to two orders of magnitude greater than the reciprocal unit cell dimensions. The Ewald sphere, having only slight curvature between points, intersects many points of a reciprocal lattice net to which it is tangent, especially when these points are extended owing to small crystal size. Similarly, within the small divergence of the electron beam there is plenty of opportunity for the wave vector to terminate on Brillouin-zone intersections that are nearly parallel to the beam direction. Thus, a condition that is rare for X-rays is practically unavoidable and highly multiple for 100-kv electrons because of their shorter wavelength. Heidenreich's comprehensive treatment (**4**) also points out that the shorter electron waves provide a better opportunity for this indirect mechanism to operate within the limited size of a coherent mosaic block. This is shown by calculating intensity as a function of crystal thickness, which is possible only in Heidenreich's treatment. The wave-mechanical approach, however, is not necessary for inferring some important consequences of this phenomenon.

Some Vector-Addition Properties of Reciprocal Lattices

Reflections do not appear if they are forbidden by general extinction rules for the space group. Thus, a body-centered

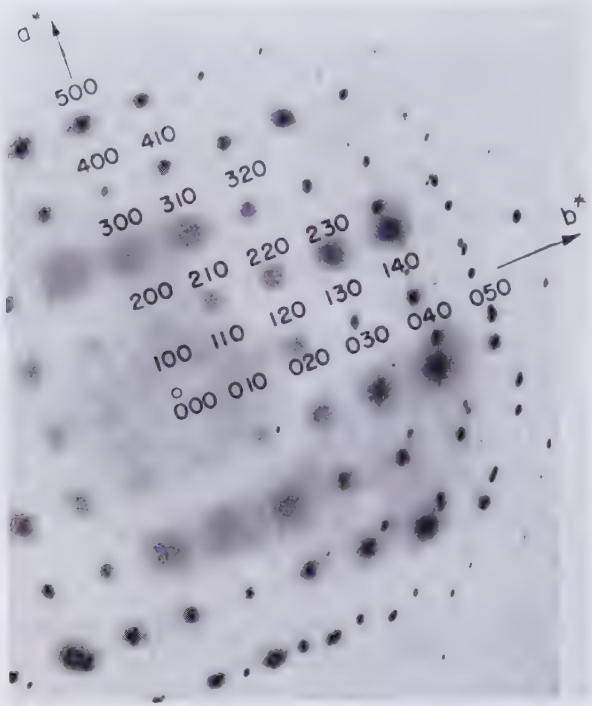


FIG. 3.—Laue Pattern of [001] Zone of Fe_3C (After Fisher (5)).

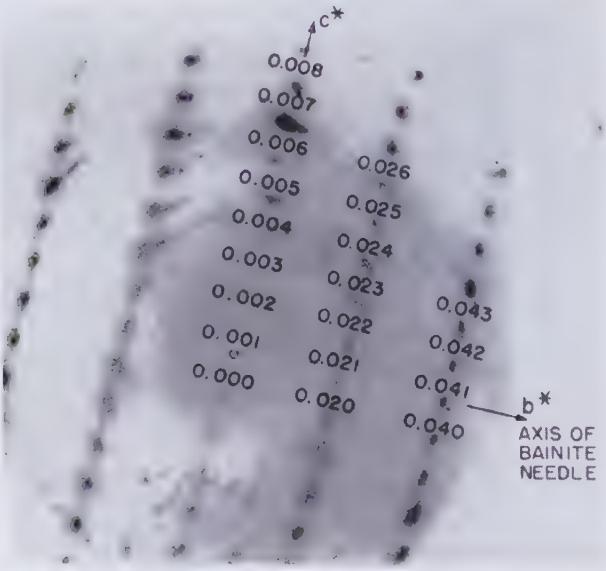


FIG. 4.—Laue Pattern of [100] Zone of Fe_3C (After Fisher (5)).

lattice allows reflections only for indices that have an even sum, and all vector additions of this special set of points are members of the same set. The same is true of the unmixed indices of face-centered lattices. Cuprite is a face-centered cubic sublattice of copper combined with a body-centered cubic sublattice of oxygen; hence multiple reflections within each sublattice will not appear to violate extinction rules. Multiple reflections between sublattices, however, will give apparent violations of extinction rules, for vector summations of the face-centered cubic and body-centered cubic sets together generate all possible reciprocal points of a primitive cubic lattice.

Screw axes and glide systems cause extinctions of certain reflections along a particular axis or within a particular plane of the reciprocal lattice. Electron diffraction patterns of such crystals generally show spots violating these extinction rules, for the forbidden reflections can be formed as vector sums from the general reflections. This is well demonstrated by two of the patterns of cementite published by Fisher (5). The cementite crystal has glide systems that forbid odd reflections along all three orthorhombic axes. Figure 3, which is reproduced from Fisher's paper, shows the [001] zone, which includes the a^* and b^* reciprocal axes, and odd reflections can be seen along both axes. Figure 4, from the same source, shows the [100] zone containing the b^* and c^* reciprocal axes. In this case there are forbidden odd reflections along c^*, but not along b^*, even though they do occur along b^* in Fig. 3. This illustrates a further rule: In a Laue pattern of a certain zone, multiple reflection may cause the appearance of forbidden reflections *only if they can be formed by vector additions within that zone*. The [100] zone of cementite has the additional extinction rule that all $(0kl)$ with odd k are forbidden, which makes the formation of $(0k0)$ with odd k by vector addition within that zone impossible. This additional restriction is not generally imposed by the theory, which requires only that the Ewald sphere intersect the initial reflection $(h_1k_1l_1)$ and the resultant $(h_3k_3l_3)$, but not necessarily the intermediate reflection $(h_2k_2l_2)$. In the case of short wavelength electrons, however, any first reflection $(h_1k_1l_1)$ of the zone makes a very small angle with the original beam, so that its reoriented reflection sphere is practically tangent to

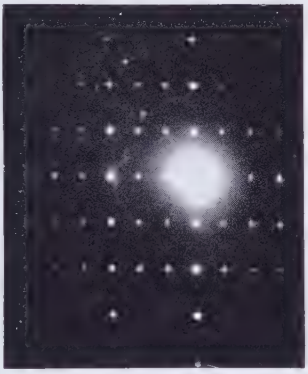


FIG. 5. Laue Pattern of [211] Zone of $M_{23}C_6$ Showing Near Uniformity of Spot Intensities.

the same zone, making it necessary for $(h_2k_2l_2)$ also to be a member of this zone.

The multiple reflection effect causes no interference with detection of order-disorder effects so long as the superlattice reflections cannot be generated by vector additions in the principal lattice.

DEGRADATION OF INFORMATION

The examples described so far cause no difficulty in phase identification. Difficulty arises, however, when one wishes to distinguish between two possible materials with the same type Bravais lattice and similar lattice parameters. This difficulty exists in distinguishing between the carbide phases $M_{23}C_6$ and M_6C com-

monly found in steels and high-temperature alloys. They are both face-centered cubic with large unit cells ($a_0 > 10$Å) and overlapping ranges of lattice parameter. In X-ray analyses they can be distinguished by moderate differences in relative intensities and an extinction rule that applies to one and not the other; thus, for example, the (420) reflection of $M_{23}C_6$ is quite prominent while the same reflection is forbidden by the M_6C structure.

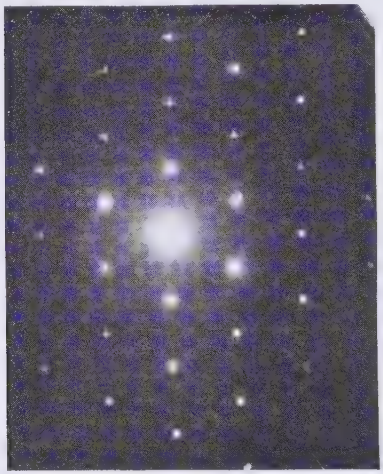


FIG. 6. Laue Pattern of Special Zone of Fe_3C Showing Spurious Extinctions for Odd $(h + k + l)$.

The multiple reflection phenomena not only fill in the forbidden reflections but also tend to strengthen the weak reflections. Figure 5 shows a Laue pattern of $M_{23}C_6$ in the [211] zone; the rectangular axes are along (111) and (022). The near uniformity of the spot intensities over the lattice is typical of electron Laue patterns. This is presumably due to strengthening of weak reflections by vector summations of strong reflections belonging to the same zone. Multiple reflections make the spot intensities more uniform than would be predicted from structure factor calculations, and thus degrade the information. This is a second consequence of multiple reflections that can explain some of the differences between X-ray and electron relative intensities. As we have seen, it is orientation-sensitive; in each crystal, whether it is the only one contributing to the pattern or whether it is contributing to a powder pattern, multiple-reflection effects can only arise as summations within the activated zone. These effects are most prominent in Laue patterns of well-populated zones, while they are less important but nonetheless observed in powder patterns.

What follows is not directly related to the subject, but it is an observed anomaly that might interest some readers of this paper.

AN OBSERVATION OF SPURIOUS EXTINCTIONS

The author would appreciate an explanation of the enigma shown in Fig. 6. It is apparently a zone spanned by (020) and (204) of a cementite plate extracted from a low-alloy steel; at least no other zones of cementite or of any other carbide identified by X-ray diffraction fit the spacings. The arrow identifies the b^* axis, which seems to be included in all cementite Laue patterns worth photographing. However, all reflections with $(h + k + l)$ odd are absent, even though they are not forbidden except along the b^* axis and the axis perpendicular to it. One of the missing reflections (122) has the highest structure amplitude of this zone (6). A given family of (hkl) has the same modulus of structure amplitude for all sign permutations of the indices; however, the structure amplitudes of the missing reflections have reversals of sign while the observed reflections do not. The same situation exists in the [001] zone, but Fig. 3 shows no spurious extinctions.

CONCLUSIONS

1. The different approaches of Renninger and Heidenreich both predict an

effect that is rare for normal X-ray diffraction but commonplace for 100-kv electron diffraction and leads to the occurrence of forbidden reflections.

2. These forbidden reflections occur only if they can be generated by vector additions of the allowed reciprocal lattice points. This restricts the effect to forbidden reflections due to glide and to screw axes.

3. Experimental data confirm these predictions and further show special restrictions for Laue patterns.

4. The mechanism also has a degrading effect on intensity information in that weak reflections are intensified and consequently there is more uniformity among spot intensities than would be predicted by the single-reflection model.

Acknowledgments:

Dr. R. M. Fisher's permission to reproduce his figures is very much appreciated. The remaining diffraction patterns were taken by Mr. A. A. Kapusta. The Renninger analysis was brought to the author's attention by Dr. Alfred Niggli of Zurich.

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X-RAY DIFFRACTION IN THE ELECTRON PROBE MICROANALYZER*

By B. H. Heise[1]

Synopsis

The electron probe microanalyzer is shown to be a useful X-ray diffraction instrument which produces a particular type of diffraction pattern known as Kossel lines. The means by which the crystal orientation and the lattice constant can be obtained from Kossel lines is also demonstrated.

The electron probe microanalyzer is primarily used in the determination of chemical composition of metallographic constituents and in the determination of composition gradients. The probe, however, has a bonus capability: the ability to perform as an X-ray diffraction instrument. Because the microscopic electron beam of the probe is able to excite a point source of X-rays, the probe may be used as a fine focus X-ray tube. If the specimen is the target in such an X-ray tube, an interesting type of diffraction—Kossel lines—results. Two applications of this diffraction, grain orientation determination and lattice constant determination, will be discussed in this paper.

Theory

A microscopic electron beam incident upon a specimen surface produces a point source of X-rays at the surface. If the specimen is composed chiefly of one element, the X-rays resulting will be mainly of wavelength $\lambda_{K\alpha}$ for that element. If the grain or crystal upon which the beam falls is large compared to the size of the electron beam, the conditions are suitable for production of a particular type of diffraction image, Kossel lines. The production of these Kossel lines will now be described.

A point X-ray source emits X-rays of the same intensity in all directions. This radiation will be diffracted whenever the Bragg conditions are satisfied. Figure 1 is a schematic drawing showing the X-ray source and a crystallographic plane whose Bragg angle is θ_1. Notice that only those X-rays lying in the surface of the cone shown in Fig. 1 will be diffracted by the plane. That is, only the X-rays in the surface of the cone strike the plane at the proper angle θ_1 to be diffracted. Since the diffracted X-rays leave the crystallographic plane at the angle θ_1, the diffracted radiation will lie in another cone coaxial with the original one but opening in the opposite direction. If a flat photographic film is placed to one side of the specimen, the trace of the cone on the film will be a conic section, a parabola, ellipse, or hyperbola. This conic section is a Kossel line.

Since part of the radiation is trans-

* Presented at a Technical Session June 26, 1961, during the Sixty-fourth Annual Meeting of the Society.

[1] Research Laboratory, The International Nickel Co., Inc., Bayonne, N. J.; now with Linde Co., Tonowanda Laboratories, Tonowanda, N. Y.

mitted through the specimen unabsorbed, the background of the film will be darkened somewhat. The Kossel line just described will be darker than the background. Other Kossel lines appear on the film which are lighter than the background. The reason for the existence of these lines can also be seen from Fig. 1. The X-rays that were diffracted must

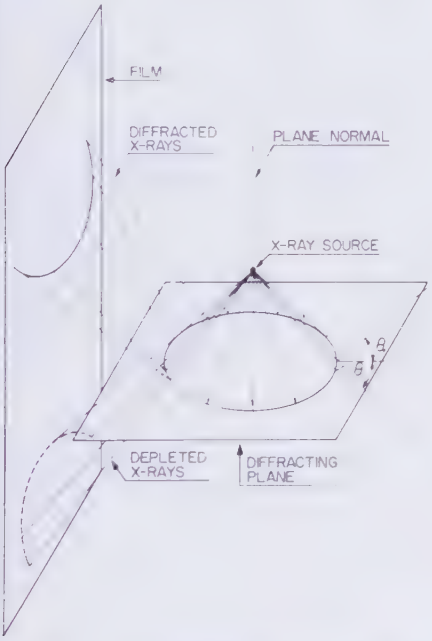

FIG. 1.—Means of Kossel Line Production. (From Heise, *Journal of Applied Physics*, Vol. 33, No. 2, p. 697, Feb., 1962.)

be subtracted from those participating in the background darkening of the film. The region of subtracted X-rays must then be the extension of the original cone of incident radiation. Therefore the light Kossel lines are also conic sections on a flat film.

In a given crystal, dozens of diffracting planes lying in many orientations are present. For each of these planes there will be a light line and a dark line appearing on the film if the film is sufficiently large. If all of the lines could be produced on a film at one time, a projection of these lines would appear as in Fig. 2, which is a stereographic projection of all of the possible diffraction lines of a single nickel grain under nickel radiation. The directions for drawing such projections have been given elsewhere.[2] Fortunately, the size of the film which can be mounted in the probe limits the area recorded to about one tenth of that shown in Fig. 2. The stereographic projection shown here is more than just a drawing exercise, however. It is useful in determining the orientation of grains, as will be demonstrated later.

SPECIMEN PREPARATION

The proper preparation of the specimen is important in the production of a good Kossel pattern. As mentioned before, the specimen must be composed mainly of one element. This is because each radiating element will produce a separate Kossel pattern, and the resulting photograph would be only a confusion of lines if many elements are present. The thickness of the specimen must lie within certain limits. If the specimen is too thin, insufficient reinforcement of the diffracted radiation will cause the lines to wash out. If the specimen is too thick, absorption effects tend to reduce the contrast between the Kossel lines and the background. The specimen must be of large grain size so that there is reasonable assurance that a grain extends entirely through the specimen. Unless the grain extends through the specimen, rediffraction of previously formed diffraction cones may result. Finally, the specimen must be in the annealed state so that not even

[2] K. Lonsdale, *Philosophical Transactions*, Royal Soc. (London), Vol. 240, p. 219 (1947).

polishing strains are present. The production of Kossel lines is very sensitive to residual cold work.

A specimen for which the thickness is only necessary to make several photographs at various s values to determine a region of reasonable contrast. If the specimen is first cut and polished in the

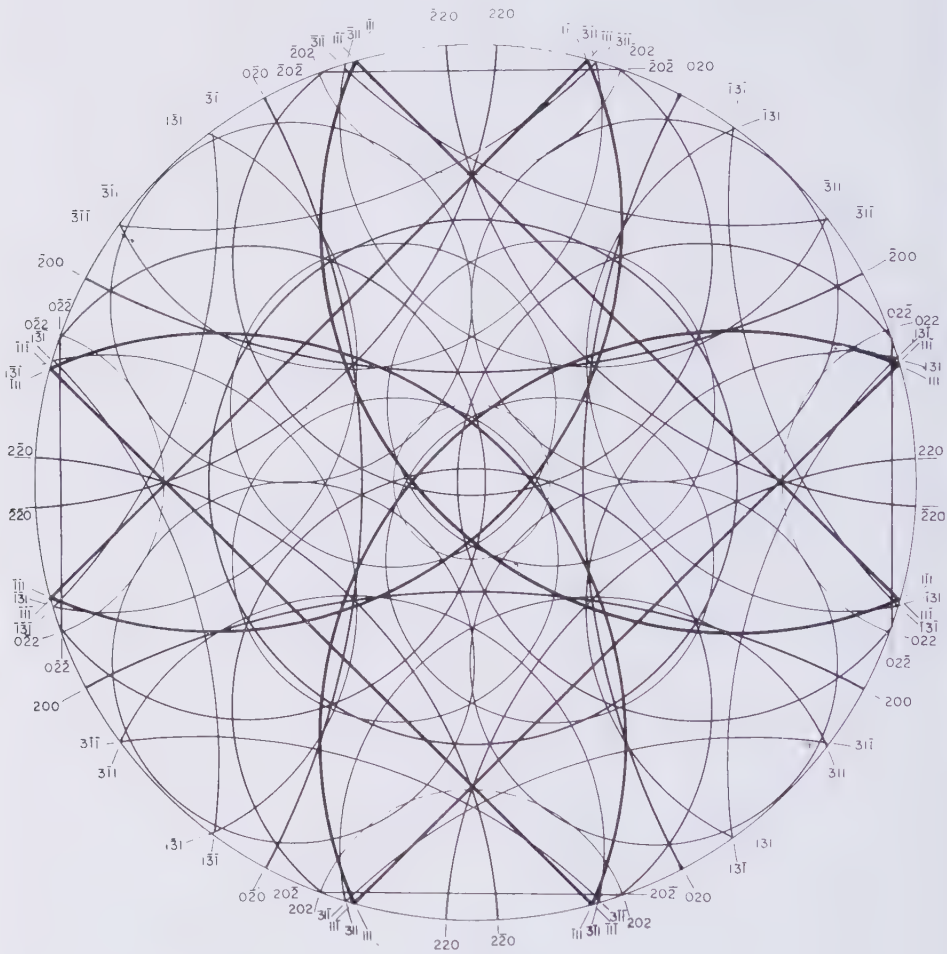

FIG. 2.—Stereographic Projection of Kossel Lines.

presents no problem is one cut as a wedge as shown in Fig. 3. The specimen thickness, t, is a function of the distance of the electron beam from the edge of the specimen, s, and the wedge angle φ. Hence the thickness can be varied by varying s. With this type of specimen it wedge shape, then annealed in vacuum at a high temperature, a large-grained, strain-free specimen of the proper shape can be produced.

The specimen used in this work was originally a $\frac{3}{16}$-in. bar of high-purity nickel. After the bar was cut and pol-

ished it was heat treated at 2000 F for 1 hr. The resulting grain size was nearly 150 μ or 6 mils, although 50 μ would have been sufficient.

PHOTOGRAPHY PROCEDURE

Since films of small dimensions could not be made to remain flat, glass photographic plates were used in these experiments. The type of plate used was an ordinary contrast lantern slide plate which had been cut into small pieces. The final plates measured $\frac{3}{8}$ by $\frac{5}{8}$ in. These were wrapped in black masking paper so that the mounting of the specimen and plate could be performed in ordinary light. The plate was placed parallel to the bottom surface of the specimen at a distance of about $\frac{1}{4}$ in. from the specimen as shown in Fig. 3. An exposure time of 5 to 10 min using an electron beam of 27 kv and 10^{-8} amp is sufficient to produce Kossel lines through a nickel specimen of 4 to 5 mils thickness.

TEST RESULTS

Figure 4 is an enlargement of a photograph taken by the method just described. Notice the geometric design reminiscent of Fig. 2. Notice also the presence of both light and dark Kossel lines.

Determination of the orientation is not difficult with the aid of Fig. 2. Notice that a fourfold symmetry axis exists in the center of the picture in Fig 4. This can only be a cube edge such as the (001) pole in the center of Fig. 2. Therefore, one particular grain of the specimen is in (001) orientation with respect to the lower surface of the specimen.

Figure 5 shows threefold symmetry such as occurs at (111) poles as shown in Fig. 2, therefore this grain is in (111) orientation with respect to the lower surface of the specimen.

Figure 6 is presented to demonstrate that the orientation can always be found so long as the Kossel line configurations about the (001) and (111) poles are kept

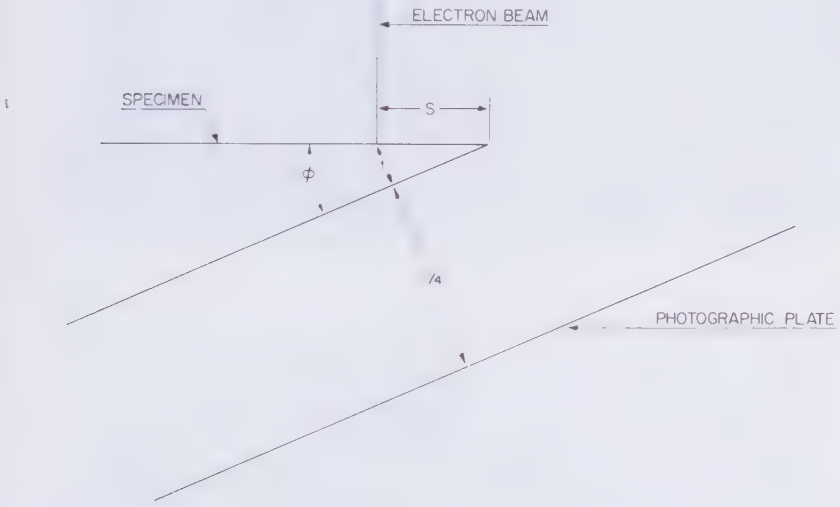

FIG. 3. Arrangement of Specimen and Photographic Plate to Obtain Kossel Lines.

FIG. 4. Kossel Lines About the (001) Pole.

FIG. 5. Kossel Lines About the (111) Pole.

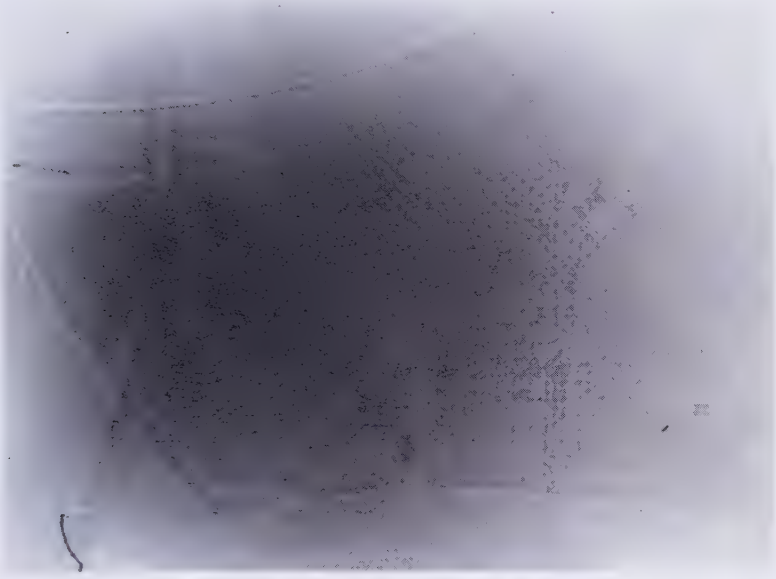

FIG. 6.—Kossel Lines About the (011) Pole.

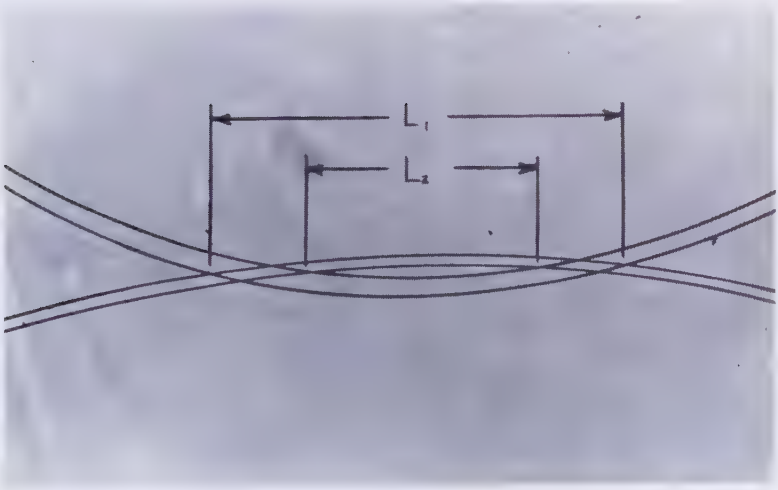

FIG. 7.—Intersection of Kossel Lines for Lattice Constant Measurement.

in mind. The orientation of this crystal is not nearly as clearly defined as in Figs. 4 and 5, yet Fig. 6 contains two of each of these types of poles to act as guideposts.

Although the lattice constant can be measured to five significant figures by means of Kossel lines, these determinations are somewhat more difficult to perform than crystal orientations. The determination depends on the existence of narrow lens-shaped figures consisting of the intersection of the Kossel lines of two high index planes. Such an intersection is that of the (004) and the (222) Kossel lines. Recall that the apex angle of a cone of diffracted radiation is dependent on the Bragg angle which, in turn, is dependent on the lattice constant. The length of one of these lens-shaped figures is a very sensitive measure of the Bragg angle because a small change in this angle is reflected as a large change in the lens length.

There are, however, certain difficulties in relating this length to the lattice constant. Since the specimen to film distance is never accurately known, the ratio of two lengths must be formed which will be independent of this distance. Furthermore, the photograph must be of such quality that the Kossel lines of the $\lambda_{K\alpha_1}$ and $\lambda_{K\alpha_2}$ radiations are resolved. That is, the lattice parameter cannot be measured to five significant figures unless the wavelength is known to this accuracy. If these Kossel lines are resolved, then a lens figure appears on the film for both the $\lambda_{K\alpha_1}$ and $\lambda_{K\alpha_2}$ radiations. Thus, the two lens lengths required become available when the lines of $\lambda_{K\alpha_1}$ and $\lambda_{K\alpha_2}$ are resolved.

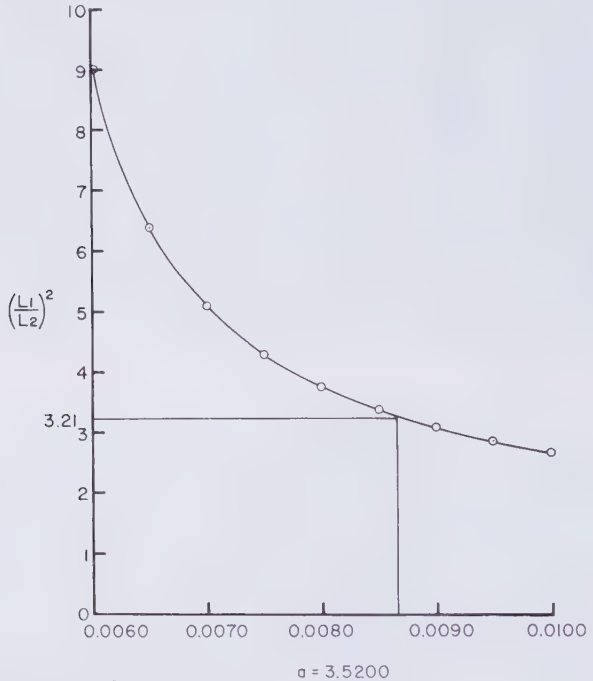

FIG. 8.—Graph for Obtaining Lattice Constant from the Square of the Length Ratio. (From Heise, *Journal of Applied Physics*, Vol. 33, No. 3, p. 938, March, 1962.)

Figure 7 is an enlargement of the lenses of intersection of (004) and (222) cones. The lines have been traced in ink to aid in reproduction, and the length of the lenses has been marked on the film.

The general formula relating the ratio of the lens length to the lattice constant is long and awkward. However, because of a fortunate placement of the lens figure on the film, the formula reduces to:

$$\left(\frac{L_1}{L_2}\right)^2 = \frac{\lambda^2_{K\alpha_2}(2a^2 - 9\lambda^2_{K\alpha_1})}{\lambda^2_{K\alpha_1}(2a^2 - 9\lambda^2_{K\alpha_2})}$$

for (004) — (222) intersections.[3] This formula is most sensitive when a graph of $(L_1/L_2)^2$ versus the lattice constant a is constructed and the measured value of L_1/L_2 is mapped onto the a axis. Figure 8 is such a plot for nickel under nickel radiation. From Fig. 7 the ratio of L_1/L_2 was found to be 1.79. The square of this number is 3.21 which corresponds to a lattice constant of 3.52865. There exists some doubt about the last figure in the lattice constant. This number does not agree with the published values; however, for this particular specimen, 3.5286 is the lattice constant.

[3] B. Heise, *Journal of Applied Physics*, Vol. 33, No. 3, p. 938 (1962).

SUMMARY

In the areas of grain orientation and lattice constant determinations, Kossel line data are as good as those obtained by any other means. Although little other work has been performed by this method, a few problems suggest themselves. Since Kossel lines are very sensitive to cold work, a delicate means of measuring cold work might be devised. Kossel lines might also be used to study coherent precipitation in metals since two Kossel patterns may appear on the photograph, one for the matrix and one for the precipitate.

CLASSIFIED BIBLIOGRAPHY ON ELECTRON PROBE X-RAY MICROANALYSIS

By Bani R. Banerjee[1]

This classified bibliography, sponsored by Subcommittee XI on Electron Microstructure of Metals of ASTM Committee E-4 on Electron Metallography, was compiled through the efforts of many scientists from several countries and includes contributions from individuals who, although not members of the ASTM subcommittee, contributed substantially to this effort.

The invaluable assistance of the following is gratefully acknowledged: Prof. R. Castaing, University of Paris; Dr. L. S. Birks, U. S. Naval Research Laboratory; Dr. K. F. J. Heinrich, Dupont; Professor J. V. P. Long, Cambridge University; Dr. T. Mulvey, A.E.I., Ltd.; Professors J. T. Norton and R. Ogilvie, Massachusetts Institute of Technology; Dr. F. Behn Riggs, Smithsonian Institute; Dr. C. M. Schwartz, Battelle Memorial Institute; Dr. R. Stickler, Westinghouse Electric Corp.: and Professor D. B. Wittry, University of Southern California.

The material is arranged as shown in the following outline:

Microprobe Analysis:

1. General, Theory
2. Techniques
3. Applications

Probe Forming:

1. Electron Optics, Theory
2. Electron Sources
3. Electron Lenses
4. Electron Scanning

Probe Phenomena:

1. Electron Penetration and Resolution
2. X-rays, Generation, Absorption
3. Backscattering
4. Heating
5. Contamination
6. Light Optical Probe Location
7. Electron Detection, Cathodoluminescence

X-ray Measurement:

1. Diffraction and Crystals
2. Detectors, and Windows
3. X-ray Spectrometers

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4. Fluorescent X-ray Analysis, Statistics
5. Nondispersive Analysis

Related Subjects:

X-ray Microscopy, Microradiography, Scanning Electron Microscopy, Kossel Line Analysis

MICROPROBE ANALYSIS

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RELATED SUBJECTS

X-ray Microscopy, Microradiography, Scanning Electron Microscopy, Kossel Line Analysis:

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P7-AHG-067